The Chemical Analysis of Waters,
Boiler- and Feed-Waters, Sewage,
and Effluents

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Sewage, and Effluents

BY

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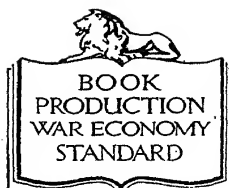
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PREFACE

This book began some years ago in the form of a practical notebook. It would not have been extended into its present form if the author's experience in the chemical industry had not convinced him of the need for a practical guide to the very wide subject of water analysis. In revising and amplifying the original notes the needs of the industrial chemist have been the first consideration. Discussion of, the principles on which the various methods are based has been reduced to a minimum, but references to original papers have been included for the benefit of those who wish to investigate more thoroughly the mechanism of any individual analysis. It has been possible to include only a fraction of the known methods; the author has exercised freedom of choice, influenced by his personal experience, and wherever possible the most straightforward methods have been chosen. In addition, most of the methods involving the use of expensive apparatus have been omitted. No·doubt p_H meters, polarographs, and photoelectric colorimeters are excellent instruments, but unfortunately they are not often to be found in works laboratories, and on the principle that they who are so fortunate as to possess them are surely familiar with their uses, it was decided that descriptions of the applications of such instruments would be superfluous in a book of this kind.

The author has drawn freely from the literature; he believes that all sources have been acknowledged by references in the text, but since the references are for the most part intended to be utilitarian, he has taken the liberty of omitting authors' initials. He wishes to acknowledge the invaluable assistance he has received from colleagues and others, too numerous to mention individually, during the period in which this work has been in preparation.

D. D.

Campden, Glos.,
September, 1943.

Dedicated to

The Memory of my Father

S. L. D.

PHYSICAL CHARACTERISTICS

CHAPTER II

SOLIDS

CHAPTER III

ALKALINITY, ACIDITY, AND p_H

CONTENTS

CHAPTER IV

HARDNESS

CHAPTER V

AMMONIA

CHAPTER VI

OXYGEN CONSUMED TESTS FOR ORGANIC MATTER

CHAPTER VII

THE BIOCHEMICAL OXYGEN DEMAND

CHAPTER VIII

NITRITES AND NITRATES

CHAPTER IX

HEAVY METALS

CHAPTER X

ALKALINE EARTH AND ALKALI METALS

CHAPTER XI

RESIDUAL CHLORINE, SALTS, FLUORINE, SILICA

CONTENTS

CHAPTER XII

SEWAGE EFFLUENTS, GREASE, FATS

CHAPTER XIII

BOILER-FEED AND BOILER-WATERS

CHAPTER XIV

THE EXPRESSION OF RESULTS

APPENDIX

Physical Characteristics

The layman invariably judges the quality of a water from its physical characteristics—colour, clarity, odour, and taste. The chemist, on the other hand, has more faith in the results of a chemical analysis of the water and he may be inclined to discount the layman's standards as being of relatively little value. A little reflection will show, however, that a report on a potable water, or on a sewage effluent, would be incomplete without a reasonably full description, at least, of the appearance of the liquid. In fact, it is not too much to say that a full description of the physical character of a sample should always be recorded as an amplification of the chemical analysis. The value of such a description in certain cases is made clear in the following paragraphs.

Colour.

Although pure water is described as colourless, it is rather unusual for a natural water or effluent to have no colour. Natural and drinking waters may vary in colour from a peaty brown to a faint white opalescence. A Lovibond tintometer may be used to measure the colour, but description will generally suffice. In this connexion it is well to remember to reserve the descriptions " very faint " and " very pale " for samples which are, in fact, almost colourless. In order to judge the colour a 100 ml. Nessler glass is filled with the sample and viewed through the depth. The standard type of glass (B. S. S. No. 612) is best, and it is an advantage to hold the glass over a clean, white, unglazed porcelain plate, facing a north light. A sheet of white unglazed paper may be substituted for the porcelain plate, and comparison of the sample with a similar tube of distilled water is helpful.

The above remarks apply to faintly coloured waters such as natural and drinking waters, sewage effluents, and boiler-feed waters. More intensely coloured solutions, such as many trade effluents and occasional boiler-waters, require different treatment. These should be allowed to settle or centrifuged before a description of the colour is attempted, since it may be due to the presence of a finely divided suspension of coloured solid in an almost colourless liquid. Such instances are commonly encountered in effluents from pigments manufacture and in rivers. Effluents from dye-works frequently merit the description " clear " in addition to their colour; sulphur-dye waste, however, is usually opaque and somewhat fluorescent, and as this class of effluent is most troublesome it is as well to bear its appearance in mind.*

Odour.

The odour of a sample should be recorded along with its colour. The description of odour is more difficult than the description of colour, so that it is fortunate that many classes of water are odourless. Some attempts have been made to measure odour. These are based on the extent to which a sample must be diluted in order to obtain an odourless solution. The dilution at which the odour is just perceptible, the threshold intensity, is recorded. It is obvious that any measurement of this kind is subject to the maximum personal error. A recent investigation by Hulbert and Feben † showed that when a number of individuals were required to assess the odours of waters by this method their results were distributed exactly according to chance. Hassler,‡ however, maintains that the measurement has some value in the hands of an experienced operator.

Odours frequently met in natural waters are those described as " peaty ", " musty ", " fish-like ", or " sulphurous ", while sewage effluents are often described appropriately as " drain-like ", unless they are of inferior quality when they may be " sulphurous " or " putrescent ". Trade effluents and

* See Appendix for descriptions of trade effluents.
† *J. Amer. Water Works Assoc.*, 1941, **33**, 1945.   ‡ Ibid., 1958.

industrial rivers may have a variety of odours, many of which are easily described.*

Suspended Matter.

The nature, abundance, colour, and state of division of any suspended matter should be described. Such characteristics are frequently aids to identification. Microscopic examination of the solid facilitates the identification of mineral matter and animal or vegetable remains.

Turbidity.

The turbidity of effluents of all kinds entering streams is frequently measured. The simplest method is to record the depth of sample through which it is just possible to see an object illuminated by diffuse daylight. Such a measure is purely relative in the absence of standardization of the object and the intensity of illumination, and the result will also vary with the operator. Watson and Weir † have described a simple apparatus which overcomes some of these difficulties. It consists of two telescopic brass tubes open at one end and fitted with glass windows at the other. The inner tube of both telescopes is also fitted with a glass window at its lower end. The inner tubes bear graduation marks along their length. The sample is poured into one of the larger tubes and distilled water into the other, when the inner tubes are slid into position. Then, on looking down one tube, a source of light is viewed through the sample, while on looking down the other tube the same source of light is viewed through distilled water. The depth of liquid looked through is adjusted by sliding the inner tube. In the apparatus described, the inner telescopic tubes are hinged together at the top so that both slide together. The apparatus is inclined at a convenient angle and the lower ends of the tubes are placed just above an opal glass plate. An electric lamp is used as source of illumination and is below the opal glass plate. The effect of a standard turbidity is obtained by placing a series of fine

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* See Appendix for descriptions of trade effluents.
† *J. Proc. Inst. Sewage Purif.*, 1937, **1**, 100.

wire gauzes, one below the other, between the opal glass plate and the lamp opposite the end of the tube containing distilled water. Now on looking down both tubes simultaneously, light travels to the eye by two paths; (1) from the lamp, through the wire gauzes and the opal glass plate, and then through distilled water; (2) from the lamp, through the opal glass plate, and then through the sample. The depth of sample through which the light must pass is then adjusted by sliding the inner tubes until the intensity of the light passing to the eye is the same from both tubes. The slide is then clamped by means of a screw and the scale reading—to which the depth of liquid corresponds—is taken. A direct measure of the turbidity of the sample, in terms of the standard turbidity produced by the gauzes, is thus obtained.

If the liquid under test is coloured, colour filters must be placed between the lamp and the telescopic tubes. The authors recommend a deep red or very deep amber filter for sewage effluents. With solutions of fairly strong colour two filters are used: a deep red one between the lamp and the bottoms of the tubes, and a pale amber one between the tops of the tubes and the eye.

Biochemical Oxygen Demand and Turbidity.

Watson and Weir have related the suspended solids content and also the biochemical oxygen demand to the turbidity. They found that with any one type of sewage effluent or with settled sewage, the turbidity plotted against the biochemical oxygen demand gave a reasonably smooth curve. This curve could then be used to determine the biochemical oxygen demand from the measure of the turbidity. The exact shape and position of the curve was found to depend on the type of treatment to which the sewage had been subjected; since the biochemical activity of the suspended solids would also depend on the same factor, as Watson and Weir actually proved, such a variation was to be expected. The authors found that when they obtained the biochemical oxygen demand from the turbidity in this way, 70 per cent of the determinations were within 5 per cent error in the B.O.D.

(biochemical oxygen demand), 20 per cent were between 5 and 10 per cent error in the B.O.D., and only 10 per cent were over 10 per cent error in the B.O.D.

Photoelectric Turbidimeter.

The same authors * also described a photoelectric turbidimeter with which more accurate measurement was possible. Their instrument contained two tubes, one for the sample and one for distilled water, which were interposed between two balanced photoelectric cells and a source of light. The photoelectric cells were wired in opposition in a circuit which contained a microammeter. The instrument was adjusted so that, with distilled water in both tubes, a reading of 100 microamps was obtained on the ammeter. The distilled water in one tube was then replaced by the liquid under test, and the resultant current read as a measure of the turbidity. This instrument gave a direct reading in percentage of the relative turbidity, relative, that is, to distilled water. Any troublesome " standard " turbidity was thus eliminated. The result was also independent of any variation in the intensity of illumination. It was often found necessary to dilute samples of sewage and sewage effluents before they could be tested by this instrument.

Wishart † has described a single-celled apparatus of simple design. He also pointed out that a measurement of this type is one of relative transparency rather than of turbidity alone. In order to determine the absolute relative turbidity it would be necessary to determine the relative transparency of a sample before and after filtration and subtract the latter value from the former. Such a procedure introduces difficulties in the presence of colloidal matter, since the size of the particles removed by filtration will depend on the size of the pores of the filtering medium. Although this suggests a possible method for the determination of the numbers of particles of different sizes which may be present in such a solution, it is certainly not worth while as a method of analysis.

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* Ibid.   † *J. Proc. Inst. Sewage Purif.*, 1937, **2**, 115.

There is some difference of opinion as to the legitimacy of the attempts to relate the biochemical oxygen demand to the turbidity of an effluent. The best answer to criticism would appear to be that a relationship has been shown to exist under certain conditions, and if this relationship can be utilized, subject to careful frequent checking, there can surely be no objection to its use.

Standards of Turbidity.

Measurement of turbidity is much more usual in America than in this country. The results are recorded in parts per million; a turbidity of x parts per million is the same as that produced by x parts of fuller's earth suspended in a million parts of water. Other suspensions of standard turbidity have been prepared from silica, Bentonite, saccharated carbonate of iron—all in water, and from barium sulphate in glycerol.

Solids

The solid matter present in waters may be divided roughly into dissolved solids and suspended matter. Sewage effluents and industrial waterways contain also some colloidal matter, so that in such cases it must be borne in mind that there is no sharp division between dissolved and suspended solids. The total solids content includes *dissolved*, *suspended* and *colloidal* matter.

Determination of Total Solids.

500 ml. of a good quality water, 100 to 250 ml. of a sewage effluent, or 50 to 100 ml. of a sewage or polluted river water should be evaporated to dryness on a water-bath. A small porcelain dish of about 4 in. diameter, previously weighed, may be used and the measured volume of sample added to it, in portions if necessary. When the evaporation is complete, the dish is removed from the water-bath and dried in an air-oven at 102° C. for four hours, finally being allowed to cool in a desiccator before weighing. In most cases it would be futile to attempt to dry to constant weight. This is particularly the case with sewages and sewage effluents which contain volatile organic matter. When such matter is present, the first weight is more likely to be nearer the truth than any subsequent weight. For those who wish to obtain the most accurate result possible it is recommended that the final drying be carried out in a vacuum desiccator over phosphorus pentoxide instead of in an air-oven at 102° C. For a critical account of methods of drying difficult substances see Horner.*

* " Determination of Total Solids in Canned Tomato Products ", *J. S. C. I.*, 1940, **59**, 74.

Determination of Mineral Ash.

If it is desired to differentiate between volatile and non-volatile matter contained in the final residue, the material is ignited. This process is preferably carried out in a muffle furnace, commencing at a low temperature and gradually increasing the temperature to about 450°–500° C. High initial temperatures and high final temperatures both lead to low results. The residue after ignition should be free from black specks.

Determination of Dissolved Solids.

Dissolved solids are determined in the same way as total solids except that the suspended matter is first removed by filtration. If colloidal matter is present the proportion of it returned as " dissolved solid " will depend on the medium employed for filtration. It will normally be least if the sample is filtered through asbestos in a Gooch crucible.

In addition to the loss of organic matter sustained during evaporation, there may also be a loss of volatile inorganic matter such as ammonium salts and carbon dioxide from bicarbonates. The determination of total solids and dissolved solids as a routine matter is of little value unless there is reason to suspect an abnormal amount of dissolved solid in the sample. This would usually be indicated by high results for some other determination.

Determination of Suspended Solids.

This determination gives more valuable information than those already described, particularly because most of the organic matter present is contained in the suspended solids in most cases.

A convenient volume of the sample is measured in a cylinder, taking care that the measured portion is representative of the sample as a whole. This is generally accomplished by vigorous shaking of the sample followed by rapid pouring of the portion required. A graduated cylinder is sufficiently accurate for the

measurement and has several advantages over a pipette in the presence of suspended matter.

A prepared Gooch crucible is used to collect the solids. " Powminco " Gooch crucible fibre is most popular for this purpose, but any good quality asbestos may be used. The Ministry of Health * recommends that the asbestos should be washed with much water to remove dust and then digested with concentrated hydrochloric acid until all the iron has been removed. It is then necessary to wash out the hydrochloric acid with successive quantities of distilled water. This, of course, is a lengthy and tedious process, and it is unnecessary with the improved grades of asbestos now available. There is a straight-sided form of Gooch crucible which is most convenient, although it is not found in general use. It is approximately $1\frac{1}{4}$ in. diameter at the top, decreasing to 1 in. at the bottom, and has a capacity of about 35 ml. It is an improvement on the more usual curved-sided form (although it is not a new design) since it combines greater stability with larger filtering area. The asbestos, previously washed with distilled water to remove dust and then made up to a fairly thick pulp with water, is added to the crucible so as to give a thin even layer over the bottom. It should be pressed down firmly with a piston-shaped glass rod or plunger while under suction on the pump. Especial attention should be paid to the firmness of the asbestos around the periphery of the crucible. The asbestos should be of such a thickness that it is just possible to see through it when the crucible is held up to the light. Prepared crucibles should be dried in the oven at 120° C. for at least three hours, removed to a desiccator and weighed immediately before use, which should be not less than one hour after placing in the desiccator.

Filtration of the sample through the Gooch crucible requires some care. If the amount of suspended matter is obviously large and more especially if it is greasy or sticky, the measured sample should be allowed to settle, when the major portion of the sample can be decanted through the crucible

and should filter with reasonable rapidity. The first third of the portion to be filtered should be allowed to filter under gravity only to prevent choking of the filter. Suction may then be applied for the filtration of the rest of the sample. The filter should be washed several times with distilled water, drained thoroughly on the pump and dried in a steam-oven at 100° C. or an air-oven at 105° C. This usually takes about four hours. The writer has found three hours at 120° C. satisfactory for routine purposes, but there is no doubt some loss of organic matter at this temperature. It is unlikely that a constant final weight will be obtained if the sample contains sewage solids. The Ministry of Health recommends that the crucible should be dried until its weight is constant to within 0·0003 gm. This is easily attained in practice.

Determination of Volatile Suspended Matter.

It is apparent that it is often of value to know what proportion of the suspended matter is of organic origin. This is determined by igniting the dry crucible after determination of the suspended solids. The operation is carried out in a muffle furnace at 450°–500° C. until no carbon remains in the residue. A crucible which has been ignited in this way should not be transferred direct to a desiccator to cool, but should first be allowed to attain a temperature of 100° C. by placing it in a steam-oven for about ten minutes, after which it may be removed safely to a desiccator and allowed to cool for at least one hour before being weighed. The object of this intermediate cooling to 100° C. is to avoid undue heating of the desiccator.

The volume of sample to be taken for the suspended solids determination must obviously vary with the sample. It is desirable that the dry residue should weigh about 0·01–0·02 gm. Results are calculated to parts per 100,000 or grains per gallon (parts per 70,000).

Modern sintered glass crucibles are not suitable for the determination of suspended matter in sewage or effluents. The time they save in preparation of a Gooch crucible is more

than lost in the time taken to clean them after use. There is also the difficult question of the grade of filter to employ.

Determination of Settleable Solids.

This test is of value when applied to sewages and effluents as a check on the efficiency of settling tanks. A portion of the sample is allowed to stand for a measured time, say two or four hours, after which the amount of suspended solid in the supernatant water is determined as above. The total suspended solid is also determined on another portion of the sample. The difference between the two values gives the " solids settleable in . . . hours ".

Determination of Suspended Solids by Centrifuge.

This test is of very doubtful value except as a purely comparative test for works control purposes. A special graduated centrifuge tube is required. As the method is a determination of weight of solid from its volume, it is necessary to have some knowledge of the apparent density of the solid. This may most easily be obtained from a series of measurements of the volume of solid settled in the centrifuge tube under definite conditions of time and speed of rotation and a corresponding series of accurate determinations of suspended solids by weight. Symons and Torrey,* working with sewage sludges, have found that the ratio of centrifuged solids (volume) to solids by weight varies with the content of volatile matter, and they have evolved a formula from which the total solids can be calculated, given the volume of centrifuged solids and the proportion of volatile matter. Such a determination is of very limited application.

Waterworks and Sewerage, 1941, 88, 106 and 195.

Alkalinity, Acidity, and p_H

Reaction to Litmus.

It is usual to record the reaction of a water to litmus. With colourless, or nearly colourless, samples this is determined by adding a few drops of the indicator to a portion of the sample in a test-tube. If the reaction is not definite, the resultant colour being neither red nor blue, a more sensitive test is to dip a strip of red or blue litmus paper into the sample to a depth of about $\frac{1}{4}$ in.; any slight change in colour is then more easily seen, since the original colour of the paper is still available for comparison. It is often necessary to wait several minutes for the colour of the paper to change. Coloured solutions may usually be tested successfully in the same way, for if the colour is of only medium strength it is seldom that sufficient of it is absorbed by the paper to mask the colour of the litmus and even strong dye wastes present little difficulty. Natural waters are seldom either decidedly acid or alkaline in their reaction to litmus. Alkalinity is usually due to lime, calcium carbonate or bicarbonate, whilst acid waters result from peaty soil or marsh-land.

Total Alkalinity.

Since methyl-orange is employed as the indicator in this determination, it is a distinct advantage to use it in admixture with a blue dye which facilitates the observation of the exact end-point. The following method incorporates such a " screened " indicator.

100 ml. of the water, filtered if necessary, are measured into a beaker and a few drops of methyl-orange solution added. This is followed by an equal number of drops of a solution of

xylene-cyanole-FF. The mixed indicator may be prepared ready for use by dissolving 1·4 gm. of xylene-cyanole-FF and 1·0 gm. of methyl-orange in 500 ml. of 50 per cent aqueous alcohol.* This will impart a green colour to the solution. 0·02 N sulphuric acid is then run in carefully from a burette until the colour of the indicator changes to a neutral grey. Excess acid will give a purple colour. Each ml. of acid is equivalent to 0·001 gm. of $CaCO_3$, hence the number of ml. of acid required gives the alkalinity of the sample in parts per 100,000 expressed as $CaCO_3$. If the result is required in terms of grains per gallon, which is parts per 70,000, it is simplest for routine purposes to take 70 ml. of the sample for titration, when the result is obtained direct from the titration figure in the same way.

. In the writer's experience, the xylene-cyanole-FF as pur-chased is not always suitable. If this proves to be the case, methylene-blue may be used instead.

Sewage effluents usually have a total alkalinity of 20 to 60 parts per 100,000, consequently it is an advantage to employ a more concentrated acid, say 0.05 N.

Trade effluents, naturally, vary a great deal in their alkalinity, up to 200 parts per 100,000 being not uncommon. A smaller quantity of sample and a more concentrated acid are advan-tageous in such cases.

It is well to remember also that alkaline reaction may arise from the presence of salts other than true bases, and that such salts may act as buffers. The interpretation to be put on alka-linity determinations under such circumstances presents something of a problem. Alkaline boiler-waters, for example, may contain phosphate, silicate and aluminate, all of which introduce errors into the total alkalinity determination. Silicate and aluminate are included in the figure for hydroxyl alka-linity (cf. p. 16). There is at present no known method where-by an accurate correction for these constituents can be applied.†
The same is true, of course, of acidity. The writer remembers

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* Hickman and Linstead, *J. C. S.*, 1922, **121**, 2501.

† Cf. *Standard Methods for the Examination of Water and Sewage*, 8th Edn., p. 96. (American Public Health Association and American Water Works Association; New York, 1936).

a case of a waste pickling liquor which, after considerable dilution, had an apparent acidity of 1000 parts per 100,000. This was due to the presence of ferric chloride. As the sewerage authority had imposed a limit of 200 parts of acidity per 100,000 (calculated as H_2SO_4) on the discharges to their sewers, the question arose as to whether the waste should be admitted or not. As the standard was set more out of consideration of the lime used at the sewage works for neutralization than possible damage to the sewer, a decision was made against the admission of the waste, since the ferric chloride, although not an acid, gave rise to an acidity which required just as much lime for neutralization as an equivalent quantity of hydrochloric acid.

Carbonate and Bicarbonate Alkalinity in the absence of Hydroxyl Alkalinity.

The neutralization of a carbonate by a strong acid takes place in two stages:

(1) $X_2CO_3 + HCl = XHCO_3 + XCl.$
(2) $XHCO_3 + HCl = XCl + H_2O + CO_2.$
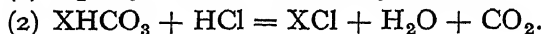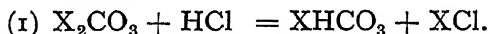
The first stage is complete at a p_H of about 8·3, and the second at p_H 4·5. By exercising a choice of indicators, therefore, it is possible to follow the two stages of the titration. Since phenolphthalein loses its pink colour when the p_H falls to 8·0 and the "neutral point" for the methyl-orange-xylene-cyanole-FF mixture is about 3·8, these indicators are suitable for the purpose.

A measured volume of the water is titrated with 0·02 N sulphuric acid, using phenolphthalein as indicator. The volume of acid required to discharge the pink colour of the indicator is noted (say x ml.) and a few drops of the screened methyl-orange solution are added. The titration is then continued until the neutral grey colour of the indicator appears. Suppose the total volume of acid added is y ml. Then, x ml. is the volume of acid required to convert all the carbonates present into bicarbonates, i.e. it is the volume required to

half-neutralize the carbonates present. The carbonate alkalinity is therefore $2x \times 100 \div$ (volume of sample taken) parts per 100,000 as $CaCO_3$. The total volume of acid required to neutralize the whole of the carbonates and the bicarbonates is y ml., hence the total alkalinity is $y \times 100 \div$ (volume of sample taken) parts per 100,000. The alkalinity due to the original bicarbonates is therefore $(y - 2x) \times 100 \div$ (volume of sample taken) parts per 100,000, expressed as equivalent $CaCO_3$.

The alkalinity of trade effluents, some sewages, industrial rivers and boiler-waters may not be due to carbonates and bicarbonates alone, but may arise also from the presence of caustic alkali, alkali hydroxides. The following method should then be applied.

Carbonate Alkalinity in the presence of Hydroxyl Alkalinity.

In such a case as this, we have, in addition to the reactions shown by equations 1 and 2, the neutralization of the hydroxyl to account for, i.e.

$$(3) \quad XOH + HCl = XCl + H_2O.$$
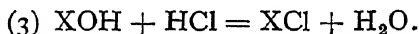
This reaction may be regarded as complete when the p_H falls to 8·3, and therefore the ml. of acid required to neutralize the caustic alkalinity and the ml. required to " half-neutralize " the carbonates will both be included in the titration with phenolphthalein. Let this volume be p ml. Let the volume of acid required to complete the titration to p_H 3·8 be q ml. Then q ml. will be equivalent to half the carbonate alkalinity, and the hydroxyl alkalinity will be equivalent to $p - q$ ml. of acid, i.e.

$$\text{Hydroxyl alkalinity} = \frac{(p - q) \times 100}{\text{vol. sample taken}} \text{ parts per 100,000.}$$

$$\text{Carbonate alkalinity} = \frac{2q \times 100}{\text{vol. sample taken}} \text{ parts per 100,000.}$$

An alternative method is to determine the total alkalinity as

described above, using the screened methyl-orange indicator and 0·02 N hydrochloric acid. Suppose this requires n ml. Then, to a fresh portion of the sample, of equal volume, add 5 ml. of a 10 per cent solution of barium chloride. This procedure removes all the carbonates and sulphates as barium salts, which are precipitated, but leaves hydroxides in solution. Add phenolphthalein indicator, and titrate rapidly with the standard hydrochloric acid. Suppose this titration requires m ml. Then

$$\text{Hydroxyl alkalinity} = \frac{m \times 100}{\text{vol. sample taken}} \text{ parts per 100,000.}$$

$$\text{Carbonate alkalinity} = \frac{(n - m) \times 100}{\text{vol. sample taken}} \text{ parts per 100,000.}$$

A similar method using strontium chloride in place of barium chloride is often preferred for boiler-water, in which the hydroxyl alkalinity may be high, as it avoids precipitation of the sulphate while removing both carbonates and phosphates as the insoluble strontium salts. A solution of strontium chloride containing 4·5 gm. of the crystalline salt per litre is required and thymolphthalein is preferable to phenolphthalein as indicator. The volume of sample taken for this determination should not contain more than 25 mgm. of hydroxyl alkalinity (expressed as equivalent $CaCO_3$). Add rapidly an excess of the strontium chloride solution and immediately place the flask on a tripod over a bunsen burner and bring the liquid to the boil as rapidly as possible. Do not allow the liquid to boil for more than a few seconds, but remove the flask from the burner and insert a stopper fitted with a soda-lime tube. Cool the flask in water, remove the stopper and add a few drops of thymolphthalein. Titrate rapidly with 0·02 N HCl until the blue colour disappears, keeping the liquid in rotation by gentle swirling of the flask during the titration. The calculation of the result is the same as for the barium chloride method.

Fair amounts of silicate, aluminate, and organic matter interfere with these methods.

Owing to the reaction

$$XHCO_3 + XOH = X_2CO_3 \cdot H_2O$$
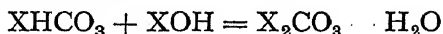
only normal carbonates can exist in the presence of hydroxyl alkalinity.

Acidity.

The determination of acidity is less often necessary than the determination of alkalinity. It is carried out simply by titration of a measured volume of the sample with standard sodium or potassium hydroxide, using litmus, methyl-orange, or phenolphthalein as indicator according to the nature of the sample and the information required (cf. p. 34). If the nature of the acid is known and further information is desired, a procedure described in any of the larger textbooks of analytical chemistry should be adopted.

Hydrogen Ion Concentration, p_H.

The p_H of a water should always be measured, since it is rare for a sample to be exactly neutral, and the p_H may be a better guide to the corrosive properties of the water than its total acidity or alkalinity. A general laboratory, dealing with all kinds of waters, should be equipped with a complete range of comparator cases such as are supplied by the leading chemical suppliers. The B.D.H. comparator is illustrated in fig. 1. The principle and method of operation are as follows.

Three test-tubes are filled with the liquid under test and placed in the spaces A, B, and C of the comparator (fig. 1a). The volume of indicator required is measured into the tube B by means of a micro-pipette which is supplied with the apparatus. It is convenient to graduate this particular test-tube by scratching a ring round it at a level corresponding with a content of 10 ml., so that the same concentration of indicator can be assured each time. The tube placed in front of this, in space E, is filled with distilled water. The apparatus contains nine sealed tubes, each of which contains a standard buffer solution at a known p_H, and a definite concentration of indicator. These standard tubes show a gradation in colour
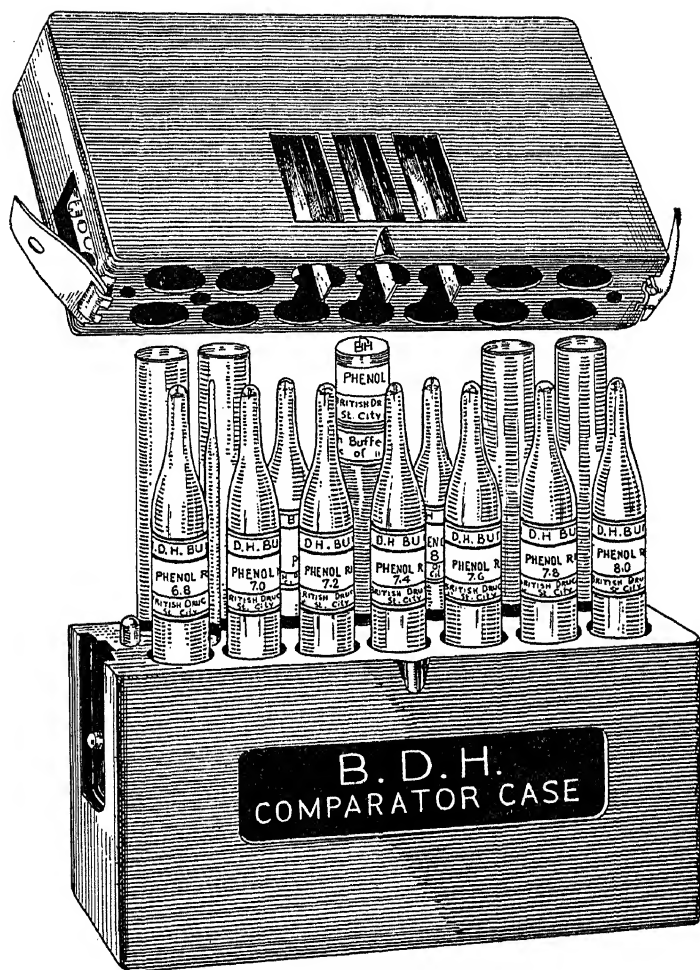
Fig. 1.—The B.D.H. Comparator

from the acid to the alkaline colour for the indicator. The p_H of the standard is marked on each of these tubes and the interval between successive standards is usually 0·2 p_H. The standards are placed in turn in spaces D and F of the comparator until one is reached which, when viewed in the direc-

tion of the arrow, just matches the colour of the sample. It
may happen, of course, that none of the standard tubes gives
a perfect match. When this happens, the standard which is
too high is placed on one side of the centre and the next
lower standard on the other side. The unknown, centre,
colour, lying between the two standards, may then be judged
to the nearest o·1 p_H.

As each comparator covers only a limited p_H range, it is
advisable when testing a sample of absolutely unknown p_H,
to test it in the first place with Universal indicator. This
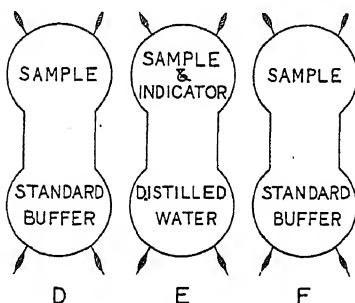
Fig. 1a.—The B.D.H. Comparator

covers the range p_H 3·0 — 11·0 and thus shows the range
within which the p_H of the sample will fall. The appropriate
indicator may then be chosen and the p_H determined to
within o·1 with the comparator. A selected list of indicators
is as follows:

Universal indicator ..	..	p_H 3·0–11·0
Bromocresol green ..	..	3·6– 5·2
Bromocresol purple	..	5·2– 6·8
Bromo-thymol blue	..	6·0– 7·6
Phenol red	..	6·8– 8·4
Thymol blue ..	..	8·0– 9·6

Samples which contain a fair amount of suspended solid
should be filtered before attempting to determine the p_H
with an indicator. Otherwise, the indicator may be adsorbed

by the solid, and a false result will be obtained. In order to filter the solution without affecting its p_H, it should be passed rapidly through a dry filter paper. The first 10 ml. of the filtrate should be rejected. The p_H of an alkaline water, such as a boiler-water, should be measured as soon as possible after the sample is drawn.

The comparator provides a simple and reliable method for the rapid determination of p_H for all waters except strongly coloured samples. These require electrical measurement.

DEEPLY COLOURED SOLUTIONS

Fluorescent Indicators.

In order to determine the alkalinity or acidity of a deeply coloured solution it is necessary to employ special methods, for the colour change of the ordinary two-colour indicator may be completely masked by the colour of the solution. There are a number of substances, of which fluorescein is the best known, which exhibit a brilliant fluorescence in alkaline solution, but not in acid solution. Such substances may be employed as indicators in acid-alkali titrations, as the extinction of the fluoresence usually takes place sharply at a definite p_H. Since the change in fluorescence is not masked by colour, the indicators are well suited to the titration of coloured trade effluents, as described by Dickinson.* He used fluorescein (p_H 7·0), umbelliferone (p_H 6·5–7·6), and acridine (p_H 5·3–7·0). Of these, acridine fluoresces in acid solution only.

Jensen † described fourteen fluorescent indicators for acidimetry, covering a p_H range of 0·0–11·0. He recommended that titrations with these indicators should be carried out in ultra-violet light. Dickinson, however, found that the three indicators mentioned above could be used in ordinary daylight, the solutions being viewed preferably against a dark background. The change in fluorescence is quite invisible in ordinary electric light, but shows up well in the light of a daylight lamp.

* *J. Proc. Inst. Sewage Purif.*, 1938, **1**, 178.   † *Z. anal. chem.*, 1933, **94**, 137

Many substances have the power to extinguish fluorescence. Weber and Savíc * asserted that this extinction is dependent solely on the properties of the fluorescent substance, and therefore, while a dye of the diphenyl type may extinguish the fluorescence of, say, fluorescein, it would not necessarily affect umbelliferone.

The method of analysis recommended is as follows.

Acidity.

Measure accurately with a pipette 25 ml. of the sample and run it into a 200-ml. conical flask. Add about 75 ml. of distilled water and a few drops of indicator solution (fluorescein or umbelliferone). Titrate with standard alkali (0·05 N), viewing the solution by reflected daylight against a dark background. The end-point is marked by the appearance of a fluorescence, brilliant green with fluorescein, sky-blue with umbelliferone.

Alkalinity.

Measure out 25 ml. of the water sample with a pipette and run it into a 200-ml. conical flask. Dilute with about 75 ml. of distilled water and add two or three drops of acridine solution. (A 0·2 per cent alcoholic solution is convenient.) Titrate with standard acid (0·05 N), viewing the solution by reflected daylight against a dark background. When the p_H falls to 7·0, a brilliant yellow-green fluorescence will appear, but will last only a few seconds. This fluorescence will become permanent when the p_H falls to 5·3.

Note.—Solutions of fluorescent indicators should be kept in the dark.

Electrometric Method for Acidity and Alkalinity.

Although fluorescent indicators are one solution of the problem of determining acidity in coloured solutions, they are not universally applicable, and some practice is required to acquire the technique. Electrometric titration with the antimony electrode is much simpler and more accurate. It

* *Z. phys. chem.*, B, **24**, 68.

cannot be employed in the presence of strong oxidizing or reducing agents.

Metallic antimony tends to dissolve in both acid and alkaline solutions and its electrode potential depends on the hydrogen ion concentration of the solution in which it is immersed. If we have two solutions of different p_H values and a rod of antimony is suspended in each, then on connecting each such electrode to a terminal of a galvanometer and connecting the two solutions by means of a salt bridge, the galvanometer needle will be deflected. If the p_H of one of the solutions is now altered so that it approaches that of the other solution, the deflection of the galvanometer needle will be reduced, reaching zero when the p_H is the same in both solutions. The apparatus required is illustrated in fig. 2. Antimony rods, 3 in. long and about $\frac{1}{4}$ in. diameter, are used as electrodes. The standard half-cell is conveniently made up in a 4-oz. wide-mouthed bottle fitted with a rubber stopper bored with two holes, one to take the antimony electrode and the other for the salt bridge. The solution for this half-cell is prepared by mixing the standard buffer solutions in the proportions indicated in Table 1 and may be of any desired p_H. The

TABLE 1

SÖRENSEN'S PHOSPHATE BUFFER

Solution A contains 11·876 gm. $Na_2HPO_4.2H_2O$ per litre.
Solution B contains 9·078 gm. KH_2PO_4 per litre.

The temperature coefficient of the buffer mixtures is negligible.

Ml. Solution A.	Ml. Solution B.	p_H
2·5	97·5	5·29
5·0	95·0	5·59
10·0	90·0	5·90
20·0	80·0	6·24
30·0	70·0	6·47
40·0	60·0	6·64
50·0	50·0	6·81
60·0	**40·0**	**6·98**
70·0	30·0	7·17
80·0	20·0	7·38
90·0	10·0	7·73
95·0	5·0	8·04

KCl

paper plug

G
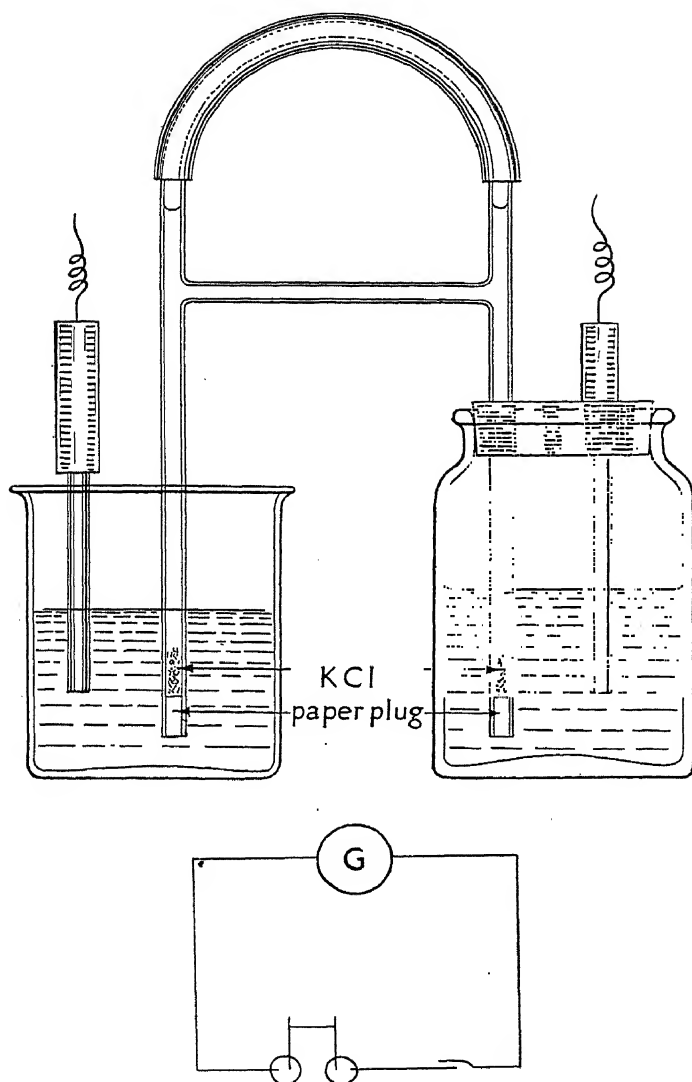
Fig. 2—Electrometric method for acidity and alkalinity

salt bridge is simply constructed from ordinary glass tubing of about $\frac{1}{4}$ in. bore, and has the form of an H. Each lower limb is plugged with a wad of filter paper and the upper limbs are connected by rubber pressure tubing. The bridge is filled with a saturated solution of potassium chloride, and it is an advantage also to introduce a few crystals of the salt. The connexion of the two upper limbs with rubber tubing

TABLE 2

PRIDEAUX AND WARD'S UNIVERSAL BUFFER SOLUTION

Titration of 100 ml. of the acid buffer solution* with 0·2 N sodium hydroxide

Ml. NaOH	p_H	Ml. NaOH	p_H	Ml. NaOH	
0·0		35·0	4·65	70·0	9·10
2·5	1·91	37·5	4·92	72·5	9·36
5·0	1·98	40·0	5·43	75·0	9·58
7·5	2·10	42·5	6·02	77·5	9·93
10·0	2·21	45·0	6·33	80·0	10·33
12·5	2·38	47·5	6·59	82·5	10·81
15·0	2·55	50·0	6·79	85·0	11·12
17·5	2·84	52·5	6·99	87·5	11·35
20·0	3·05	55·0	7·24	90·0	11·47
22·5	3·38	57·5	7·51	92·5	11·64
25·0	3·75	60·0	7·95	95·0	11·75
27·5	3·92	62·5	8·35	97·5	11·84
	4·22	65·0	8·68	100·0	11·94
32·5	4·33	67·5	8·90		

Data according to Britton and Robinson (*J. C. S.*, 1931, 458)

helps to minimize loss of the bridge solution and also serves as a convenient handle by which to hang the bridge when it is not in use. One of the lower limbs of the salt bridge is passed through the rubber stopper of the standard half-cell to make contact with the solution of known p_H.

The solution to be titrated (here considered to be acid) is measured into a beaker (250 ml. squat form is convenient) and diluted to a convenient volume with distilled water. The

* For composition see text.

other antimony electrode is suspended in this and held by a clamp. The free limb of the salt bridge is also dipped into this solution. The level of the solution in the standard half-cell should always be slightly higher than that in the beaker, so that if any liquid siphons through the salt bridge the direction of flow will prevent contamination of the standard buffer solution or of the bridge solution. The circuit is completed according to the diagram shown. Contact with the antimony is conveniently effected by the device illustrated in fig. 3. Standard alkali solution is then run from a burette into the unknown solution 1 ml. at a time, stirring vigorously after each addition, pressing the key, and noting the deflection of the galvanometer needle. As soon as this begins to decrease significantly, the addition of the alkali is reduced to 0·1 ml. at a time and finally to one drop or less. (Less than one drop can be taken from a burette by opening the tap carefully until, say, a half-drop hangs on the end of the jet and washing this into the vessel by a stream of distilled water from a wash-bottle.) The titration is completed as soon as the deflection of the galvanometer needle is reduced to zero. A slight excess of alkali will cause a deflection in the opposite direction.
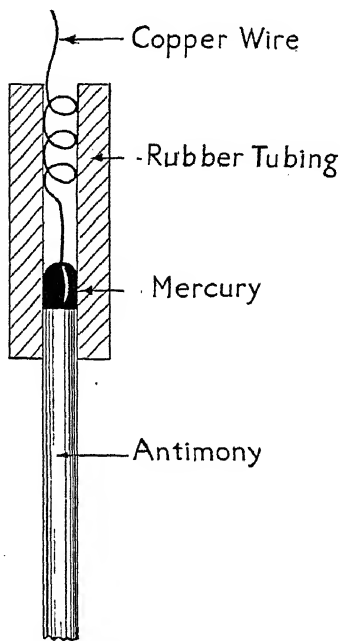
Fig. 3.—Contact with antimony electrode

The advantages of this method are numerous. It is more accurate than using an indicator and it is not subject to the personal error involved in the judgment of a colour change. The titration can be carried to any desired p_H by choice of a suitable buffer solution for the standard half-cell. The same

assembly can be used for the titration of acids or alkalis, while the presence of colouring matter in the solution to be titrated is of no consequence.

After use the electrodes should be washed thoroughly in a jet of distilled water, and occasional cleaning with fine emery paper is recommended.   For further information on the chemistry of the antimony electrode the researches of Britton and Robinson * should be consulted.

Determination of   Titration.

According to Sand † the idea of determining p_H by titration must be attributed to G. Roeder.   It follows as a natural corollary of the method of acidimetry described above.   In this case the p_H of the standard half-cell, or reference solution, is varied until the galvanometer needle gives no deflection. The principle of the method and the assembly of the apparatus are exactly the same as the above, except that the positions of the solutions are reversed, the unknown solution being placed in the bottle.

In order to prepare a continuous series of solutions of known p_H a universal buffer solution is required.   The author has found the universal buffer solution of Prideaux and Ward suitable for the purpose.   An acid buffer solution is prepared, containing phosphoric acid, boric acid and phenylacetic acid, each 0·04 M.   When this is titrated with 0·20 N sodium hydroxide solution, the p_H of the mixture is obtainable from a graph constructed from the data in Table 2 (p. 24).   In order to determine the p_H of a solution it is poured into the bottle in the apparatus described and an antimony electrode and the salt bridge dipped into it.   100 ml. of the acid buffer solution are pipetted into the beaker, the other antimony electrode and the other end of the salt bridge suspended in it, and the circuit completed.   0·20 N sodium hydroxide is then run from the burette into the acid buffer solution exactly as described for the determination of acidity.   When the galvanometer needle no longer deflects when the key is de-

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* *J. C. S.*, 1931, 458.

† *Electrochemistry and Electrochemical Analysis*, Vol. III, p. 112 (Blackie, 1941).

pressed, the p_H is the same in both solutions. The value is obtained by observing the ml. of caustic soda solution required for the titration and converting this quantity to p_H by means of the graph.

This method has been found to work very well within the limits of p_H 2–12, a range quite wide enough for water analysis, and provided also that there is no considerable concentration of strong oxidizing or reducing agent present. In this latter connexion, the method was found not to be affected by a suspension of lead chromate present in the effluent from a chemical works. As a check, the author has used this method to determine the dissociation constants of several weak acids. p_K (= − log dissociation constant) for hydrocyanic acid was found to be 9·55–9·65, compared with previous values of 9·41,[*] 9·5–9·6, and 9·35.[†] p_K for hydrazoic acid was found to be 4·88, compared with 4·97,[‡] 4·74, 4·59,[§] and 5·10[‖]. No definite results could be obtained for chromic acid, in agreement with the experience of Britton and Robinson.

[*] Harman and Worley, *Trans. Farad. Soc.*, 1924, **20**, 502.
[†] Cf. Britton and Robinson, ibid.
[‡] Britton and Robinson, ibid.
[§] Hughes, *J. C. S.*, 1928, 502.
[‖] Oliveri-Mandala, quoted by Britton and Robinson.

Hardness

The determination of the hardness or soap-consuming power of water, for industrial and domestic supplies, is one of the oldest tests. The method for its determination was devised by Clark,* and it is still in use, with very little modification, to this day. The hardness is due to the presence in the water of salts of calcium and magnesium, and to a less extent to salts of zinc, iron, and aluminium, and the most accurate method for the computation of the hardness is its calculation from the concentrations of calcium and magnesium (cf. Chap. XIV). Any such calculation, however, involves two rather lengthy determinations, and it is sufficient for most purposes to employ Clark's method, which consists simply of the addition of a standard soap solution to a measured volume of the water until the calcium and magnesium have been completely precipitated and sufficient excess soap has been added to form a permanent lather in the solution. The hardness thus measured is, strictly speaking, " soap-consuming power ", and it is as well to bear this fact in mind.

Determination of Total Hardness.

The reagents required for the determination are:

(1) *Standard Calcium Chloride Solution.*—Dissolve 0·5 gm. of pure calcite in dilute hydrochloric acid contained in a conical flask. Cover the flask with a watch-glass to avoid loss of the solution as spray. When solution is complete, transfer

* *Chem. Gaz.*, 1847, **5**, 100.

the contents of the flask to a 500-ml. graduated flask, using freshly-boiled and cooled distilled water to wash out the conical flask and the watch-glass. Add sufficient litmus to colour the solution and neutralize it by adding dilute ammonia. Then make up to 500 ml. with freshly-boiled and cooled distilled water. The solution should then be stored in a stoppered container.

(2) *Soap Solution.*—Shake 100 gm. of pure powdered castile soap with a litre of 80 per cent alcohol (diluted industrial methylated spirit is of sufficient quality) and allow the mixture to stand for at least 18–24 hours. Then decant the clear solution into a stoppered bottle. This is the stock solution and is approximately 10 times the strength of the standard solution required. It is advisable to dilute approximately 100 ml. of this solution to 500 ml. with 80 per cent alcohol, which gives a solution approximately twice as concentrated as is required. Measure 50 ml. of boiled distilled water into a bottle of 250–300 ml. capacity and fitted with a ground-glass stopper, and run in the soap solution from a burette a drop at a time, shaking the bottle vigorously after each addition until a lather is produced which remains permanent for five minutes with the bottle laid on its side. Note the volume of soap solution required. This is the " lather factor " for the solution, i.e. the volume of solution required to give a permanent lather with a water of zero hardness, and it will generally be found to lie between 0·25 and 0·7 ml. Now measure into the bottle, after rinsing with distilled water, 10 ml. of the standard calcium chloride solution and add 40 ml. of boiled distilled water and repeat the titration in the same way. From the volume of soap solution required deduct the lather factor and the net volume should then be approximately 5 ml. Then dilute x ml. of the soap solution to 1 litre with 80 per cent alcohol, in which $x = 1000 \times$ vol. of soap solution required for titration ÷ 10. Then repeat the determinations described above until the volume of the diluted soap solution required for the second titration is exactly 10 ml. *plus* the lather factor.

1 ml. of the standard soap solution is then equivalent to

1 ml. of the calcium chloride solution, which is in turn equivalent to 1 mgm. of calcium carbonate.

(For the benefit of those who may have to carry out only occasional determinations of hardness, accurately standardized soap solutions can be purchased ready prepared.)

The determination of the hardness of a water is carried out in the same way as the standardization of the soap solution. The volume of the sample taken for the determination depends on its hardness and also on the units in which it is desired to express the results. 1 degree of hardness on Clark's scale is 1 grain of $CaCO_3$ per gallon (1 part in 70,000); if the results are required on this scale, then 70. ml. or a fraction of 70 ml. of the water should be taken. If " parts per million " are required, 50 ml. of the sample should be taken. The soap solution is added to the sample 1 ml. at a time from a burette and the bottle is shaken thoroughly after each addition. When a lather is obtained which remains permanent for 5 minutes with the bottle laid on its side, the end-point has been reached or passed. The determination is then repeated and the end-point approached more cautiously so as to determine it to within 0·1 ml. In the presence of magnesium salts there appears a false end-point, or " ghost-point ", at which a fairly stable lather forms, but it does not usually last for five minutes. However, when the end-point appears to have been reached, it is usual to add a further 0·5 ml. of the soap solution, when, if the end-point noted was in fact the ghost-point, the lather will be found to break down again, whereas if it was the true end-point, the lather will remain permanent. The author has found that the end-point can be detected quite simply by sound; before it is reached the sound of the solutions being shaken in the bottle is quite sharp, but as soon as excess soap solution has been added the sound is dull or muffled. This, of course, is used merely as a guide when carrying out a titration.

If more than 15 ml. of the standard soap solution are required, the titration should be repeated using a half or a quarter of the volume of water and making up to 50 ml. or 70 ml., as the case may be, with boiled distilled water.

The result is calculated:

(*a*) in grains per gallon (Volume. of soap solution required
— lather factor) × 70/(Volume of sample titrated);

(*b*) in p.p.m. (Volume of soap solution required — lather
factor) × 1000/(Volume of sample titrated).

The lather factor must be determined frequently, using freshly-boiled and cooled distilled water. Occasional checking of the soap · solution against the standard calcium chloride solution must not be overlooked.

Determination of Hardness by Potassium Palmitate.

The end-point to this titration is marked by a colour change and hence it has found considerable favour. Kitto * recommends the use of a " blank " end-point. His procedure is described below. The method is generally known as Blacher's method.

Standard potassium palmitate solution is prepared by dissolving 26·5 gm. of potassium palmitate in 800 ml. of warm 90 per cent alcohol and adding 500 gm. of glycerol and 0·2 gm. of phenolphthalein. Approximately 100 ml. of a 20 per cent solution of potassium hydroxide in alcohol are then added, followed by the careful addition of a further quantity of the same solution until a very faint pink colour is produced. The palmitate solution is then standardized against calcium chloride solution (cf. p. 28).

Prepare an " end-point blank " from 100 ml. of distilled water by adding 0·5 ml. of 1 per cent alcoholic phenolphthalein solution and then sufficient 0·1 N sodium hydroxide to produce a pink colour. Then add 0·1 N hydrochloric acid carefully until the solution is just decolorized and add a further drop in excess. Run in the standard palmitate solution from a burette until the solution has a strong red colour and note the volume of palmitate required.

Neutralize 100 ml. of the water sample to methyl-orange with 0·1 N hydrochloric acid, bubble air through it to remove

carbon dioxide, and then add o·5 ml. of 1 per cent phenol-phthalein solution. Add o·1 N sodium hydroxide until a pink colour is produced, then o·1 N hydrochloric acid to discharge the pink colour and one drop in excess. Titrate with standard palmitate solution until the red colour produced matches that of the blank. Titrations should be carried out in conical flasks, and the matching of the test solution with the blank is done by holding both flasks some distance from the eyes over a white tile in such a way that they are viewed by reflected rather than transmitted light. The blank may be rendered turbid to match the test solution by adding a little kaolin. The titration figure less the volume of palmitate added to the blank × 10 is the hardness in p.p.m. To obtain " grains per gallon " or " degrees Clark " take 70 ml. of the sample for the titration, when the result is given by " ml. required — ml. in blank ". It is not strictly correct to quote results obtained by this method as " degrees Clark ".

Determination of Magnesium Hardness.

In order to determine the hardness due to magnesium as distinct from calcium salts, a measured volume of the sample is treated with sodium oxalate solution to precipitate the calcium, after which the residual hardness is determined by the palmitate method described above.

Pipette 200 ml. of the sample into a conical flask and add a few drops of methyl-orange indicator. Add o·1 N hydro-chloric acid until the solution is just pink and then add two drops in excess. Boil the solution gently for five minutes to expel carbon dioxide. While the solution is still boiling, add 5 ml. of saturated sodium oxalate solution, stir well, and cool the mixture. It is not necessary to filter off the precipitate.

Add 1 ml. of 1 per cent phenolphthalein solution and pro-ceed with the addition of sodium hydroxide and hydrochloric acid as described in the previous section. An end-point blank should be prepared from 200 ml. of distilled water. The magnesium hardness—in terms of p.p.m. $CaCO_3$—is given by

(Ml. palmitate solution required — ml. required for the blank) × 5.

Determination of Temporary Hardness.

By definition, the temporary hardness is that which is destroyed by boiling the water. It may be determined simply by boiling a measured volume of the water for 15 minutes in a conical flask, cooling, making up to the original volume with boiled distilled water, and determining the hardness of the solution thus obtained. The temporary hardness is the difference between the results for the raw and boiled waters.

Non-carbonate Hardness.

If the total alkalinity of a water is calculated as calcium carbonate, it follows that if the whole of the hardness of that water is due to dissolved carbonates and it is calculated as calcium carbonate, then the two values expressed in the same units should be equal. If the hardness is greater than the alkalinity, salts other than carbonates must be responsible for the extra hardness, but if the alkalinity is equal to or greater than the total hardness, there is no non-carbonate hardness. Non-carbonate hardness may be determined directly by the use of a solution of sodium hydroxide 2 gm. and anhydrous sodium carbonate 2·65 gm. in a litre of distilled water. 200 ml. of the water sample are measured into a conical flask and boiled for 15 minutes. 200 ml. of distilled water in a similar flask are also boiled at the same time. This procedure removes dissolved carbon dioxide. 25 ml. of the mixed solution of sodium hydroxide and carbonate are then pipetted into each of the two flasks and the solutions are boiled for a further 10 minutes. After cooling, each solution is transferred to a 200-ml. graduated flask and made up to volume. The quantity of alkaline reagent remaining in each solution is then determined by titration of 50 ml. of the filtered solution with standard sulphuric acid solution (N/50), using methyl orange as indicator. The difference between the two titrations is a measure of the alkali reagent required to decompose the calcium and magnesium salts, other than carbonates, present in the water. If more than half the alkali

reagent is found to have been used, the determination should be repeated on a diluted sample.

The result is calculated:

(a) In p.p.m.,

non-carbonate hardness = (ml. difference between H_2SO_4 titrations) × (normality of H_2SO_4) × (equivalent wt. of $CaCO_3$, = 50) × 200/50 × 1000/(volume of sample taken) p.p.m. $CaCO_3$.

(b) In grains per gallon,

non-carbonate hardness = (ml. difference between H_2SO_4 titrations) × (normality of H_2SO_4) × (equivalent wt. of $CaCO_3$, = 50) × 200/50 × 70/(volume of sample taken) gr. per gal. $CaCO_3$.

FREE CARBON DIOXIDE

Any carbon dioxide present in a water in excess of that required to convert all the alkaline earth or alkali carbonates to bicarbonates exists as CO_2 in solution. In this state it is sometimes termed " aggressive " CO_2 as it accelerates corrosion, presumably by preventing the formation of protective carbonate scales.

The following method may be used as a guide.

Estimation of Free Carbon Dioxide.

A special sample should be taken for this determination. The bottle should be filled completely with the sample, which should then be maintained at a temperature below that of the water from which it is taken.

Pipette 100 ml. of the sample into a 100-ml. Nessler glass and add 1·0 ml. of phenolphthalein solution (0·5 per cent in 50 per cent aqueous *neutral* alcohol). Titrate rapidly with N/100 sodium hydroxide until a faint permanent pink colour is produced.

The result is given by (ml. NaOH required) × 4·4 = p.p.m. CO_2.

The result obviously requires correction if mineral acids are present, and also if appreciable quantities of iron and aluminium salts are present. These latter interfere by slow reaction with the sodium hydroxide, rendering the end-point indistinct. If the sample is acid to methyl-orange, determine the extent of this acidity by titration with methyl-orange as indicator and ascribe this to mineral acid. Calculate as CO_2 as above, and deduct from the free CO_2 as determined. The presence of iron and aluminium salts may be apparent from the formation of precipitates during the titration. The best way to correct for them is to calculate the ml. of the sodium hydroxide required to precipitate the iron and aluminium salts as hydroxides from the concentrations of these metals found to be present.

Only when the p_H of the sample is greater than 6·0 can the method be applied with reasonable certainty without correction.

Ammonia

Very few waters are entirely free from ammonia in some form. It is one of the products of the breakdown of organic matter by bacteria and it is a by-product of animal metabolism, so that its presence in quantity in a natural water is often due to sewage pollution. Ammonia or an ammonium salt is used in the newly-developed ammonia-chlorine treatment for water supplies (see e.g. Committee Report on the Chlorine-Ammonia Treatment of Water Supplies);* here it is converted into one or other of the chloramines. Any ammonia present in a water prior to chlorination is also converted to chloramine. Ammonia is so widely used in industry and in the household that it is always found in fair quantity in sewages and effluents. Ammonium carbamate would in any case arise from the presence of urea.

The term " free and saline ammonia " is applied to all the ammonia which is liberated by distillation with very dilute alkali, and it is determined quite simply as a routine analysis. It is usual to follow this determination by an assay of the " albuminoid ammonia " or more correctly " albuminoid nitrogen ". This is the term used to describe the ammonia which is liberated from organic matter by oxidation by potassium permanganate in strongly alkaline solution. It is perhaps the most sensitive test for pollution which has yet been devised and should be applied invariably to samples whose purity is suspect.

Nessler Reagent.

This solution is prepared substantially according to the instructions of Wanklyn and Chapman.†　70 gm. of potassium

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* *J. Amer. Water Works Assoc.*, 1941, **33**, 2079.　† *Water Analysis*, 5th Edn., p. 33.

iodide are dissolved in about 400 ml. of water and a saturated (5 per cent) solution of mercuric chloride is added with stirring. After 500 ml. of this solution have been added, further additions are made more cautiously until the scarlet precipitate which forms and redissolves on each addition just begins to be permanent. A solution of 320 gm. of caustic potash or 240 gm. of caustic soda in about 500 ml. of water is then stirred in, after which the volume is made up to 2 litres with distilled water. A little more mercuric chloride solution is then added so that a permanent precipitate is obtained. After standing overnight the solution is decanted into a Winchester bottle and stored in the dark. A smaller dark glass bottle should be used to contain a portion of the solution in current use.

Ammonia-free Distilled Water.

The preparation of this material is frequently troublesome; a good quality water is required as raw material. Two methods of treatment may be employed. A little sodium carbonate added to the water to be distilled will help to drive off the ammonia it contains in the first fraction of the distillate; the distillate should be collected only when it is found to be free from ammonia when tested with the Nessler reagent. Alternatively, the ammonia may be retained in the still by adding a trace of sulphuric acid and a crystal of potassium permanganate to the water to be distilled. The pink colour of the permanganate should persist throughout the distillation and care must be taken to avoid undue concentration of the residue in the still. If this is not done the permanganate and acid will react with the chlorides naturally present in the water and chlorine will be produced. For the same reason any deposit of manganese oxides which may form in the still must be removed periodically. Of the two methods, distillation with acid permanganate generally gives most satisfactory results. It is the method recommended by the Association of Official Agricultural Chemists.

Determination of Free and Saline Ammonia.

A standard solution of ammonium chloride is prepared by dissolving 3·821 gm. of the reagent-quality salt in 1 litre of ammonia-free distilled water; the solution then contains 0·001 gm. of nitrogen in the form of ammonia (NH_3—N) per ml. From this stock solution, a dilute solution containing 0·00001 gm. NH_3—N per ml. is prepared for use in the preparation of colour standards. Not more than three-quarters of either solution should be used and both should be examined regularly for mould or algal growths.

A distillation apparatus is required for the determination. The flask should have a capacity of $1\frac{1}{2}$ to 2 litres. A distilling flask may be used, but it is more convenient and in many ways better to use an ordinary round-bottomed flask and fit it with an anti-splash head. The condenser may be of any convenient form, but a multiple condenser is a decided advantage if many determinations are to be done. The corks used in the assembly of this apparatus should be wrapped in tin-foil. This preserves them and also prevents pieces of cork from falling into the flask or into the distillate. It is necessary to free the apparatus from ammonia immediately before use. The flask is rather more than half filled with ordinary distilled water and this is distilled until the distillate is found to be free from ammonia on Nesslerization.

The volume of sample to be taken for distillation cannot be stated very definitely, but the following may be taken as a guide.

Tap water	up to 500 ml.
Good quality sewage effluents and streams	20–50 ml.
Ordinary sewage effluents and polluted rivers	10–20 ml.
Sewage, &c.	5 ml.

It is inadvisable to take less than 5 ml. of a sample, as any smaller quantity cannot possibly be representative of the whole.

After the apparatus has been freed from ammonia, the

measured volume of the sample is added to the contents of the flask as soon as the latter is sufficiently cool to handle. The cork is then refitted into the flask as quickly as possible and the distillation is begun. 200 or 250 ml. of the distillate should be collected as the first fraction, collecting either in a large Nessler glass or in a special form of graduated flask (a small squat type with a wide neck). Further 50 ml. fractions are then collected until one is obtained which is practically free from ammonia. Three fractions are usually sufficient— i.e. one of 200–250 ml. and two of 50 ml.

A series of standards is prepared from the dilute ammonia solution. A number of matched Nessler glasses of 50-ml. capacity are required and are conveniently mounted in a stand consisting of a long piece of wood about 1 in. thick and with a number of holes bored through it, each big enough to take the base of a Nessler glass. Approximately 47 ml. of ammonia-free distilled water are added to each tube and this is followed by a volume of the standard dilute ammonium chloride solution measured accurately from a small-capacity graduated pipette. A suitable range of standards would contain 0, 0·2, 0·4, 0·6, 0·8, 1·0, 1·2, 1·4, 1·6, 1·8, 2·0, 2·2 ml. of this solution. The contents of each Nessler tube are then made up to the 50-ml. mark with ammonia-free distilled water.

After mixing the first fraction of the distillate by inversion of the container, 50 ml. are poured out into a Nessler tube. 50-ml. portions of the other fractions should also be taken, but usually they will have been collected in 50-ml. fractions. 2 ml. of the Nessler reagent are then added to each of the standards and to each 50-ml. portion of the distillates, and the contents of each tube are mixed with a glass plunger. After not less than two minutes, the colours developed in the distillates are compared with those of the standards, matching to the nearest 0·1. If any one of the fractions of distillate develops a colour deeper than that of the highest standard, 26 ml. of the Nesslerized solution should be measured and diluted to 50 ml. with ammonia-free water. It should then be matched to the nearest standard and the value of that standard—expressed in ml. of the dilute ammonium chloride

solution—multiplied by 2 to correct for the dilution. The following example will serve to illustrate the determination.

Example.

10 ml. of sewage were taken for distillation. The distillate was collected in portions of 250 ml., 50 ml., and 50 ml. Of the 250-ml. fraction, 50 ml. was taken for Nesslerization. The colour developed in this solution was deeper than that of the highest standard, but on diluting 26 ml. to 50 ml., the resultant solution matched the standard containing 1·6 ml. of ammonium chloride solution. The first 250 ml. of distillate therefore contained the equivalent of 1·6 × 2 × 5 = 16·0 ml. of ammonium chloride solution. The second fraction of distillate, 50 ml., matched the standard containing 0·8 ml. of ammonium chloride solution; the third fraction, 50 ml., gave a colour intermediate in depth between those of the 0·2 and 0·4 standards and was judged to contain the equivalent of 0·3 ml. of the standard ammonium chloride. · Hence, 10 ml. of the sample contained the equivalent of 16·0 + 0·8 + 0·3 = 17·1 ml. of the ammonium chloride solution, 1 ml. of which contains 0·00001 gm. of NH_3—N. The sample contained, therefore, 17·1 × 0·00001 gm. of NH_3—N in 10 ml., or 1·71 parts per 100,000, or 17·1 p.p.m. of nitrogen in the form of ammonia.

Determination of Albuminoid Nitrogen.

8 gm. of potassium permanganate is dissolved in a litre of hot water in a porcelain basin. A solution of 150 gm. of sodium hydroxide in 500 ml. of water is then added and the solution is evaporated to a volume slightly less than 1 litre. When cold, the volume is made up to 1 litre with ammonia-free distilled water.

35 ml. of this alkaline permanganate solution are added to the residue in the distillation flask after distillation of the free and saline ammonia, which should measure about 400 ml.; the flask is again heated, and a further two or three fractions are collected. The total volume of these fractions should be between 200 and 250 ml. The various fractions, or aliquots of

them, are Nesslerized as described above and the result calculated in the same way, but returned in this case as "albuminoid nitrogen".

It is generally useless to attempt to distil all the albuminoid ammonia, as it will continue to be given off in decreasing quantities for an indefinite period.

Notes on Ammonia Distillations

The addition of alkali to the solution for distillation is normally unnecessary as the glass vessel renders the solution sufficiently alkaline. Any carbonates present in the sample will also assist the liberation of ammonia. If there is hydrogen sulphide present in the sample or if the sample is acid in reaction, the Ministry of Health recommends the addition of two or three drops of approximately $\frac{1}{2}$ N sodium carbonate solution to the contents of the distillation flask. The addition of 1 ml. of M/20 disodium hydrogen phosphate solution has also been recommended and the author has found this to be quite satisfactory. When hydrogen sulphide is present the Association of Official Agricultural Chemists recommends a preliminary acidification and boiling of a portion of the sample to remove the H_2S; the solution is then neutralized, made up to a volume, and an aliquot portion taken for distillation.

The above methods are not intended for the determination of ammonia in trade effluents which contain large quantities of ammonium salts. For such effluents the usual distillation into standard acid should be employed.

Oxygen Consumed Tests for Organic Matter

.A variety of determinations must be included under this heading, but although they vary considerably in the reagents employed and in their operations, they all have the object of measuring the amount of organic·matter present by determining the weight of oxygen which is required for its oxidation under controlled conditions. The determination of biochemical oxygen demand (B.O.D.) is a test of this type, but in order to avoid too cumbersome a section, it has been assigned a separate chapter. The organic matter is rarely oxidized completely in these determinations and it is therefore necessary to work with standard concentrations of reagents and to allow the reaction to proceed for a definite time at a standard temperature. The following standard methods are in use.

Determination of Oxygen absorbed from Acid Potassium Permanganate in 4 Hours at 80° F. (26·7° C.).

(a) *Using* N/80 *Potassium Permanganate.*

This is the method most widely used in this country for the examination of sewage, effluents, and trade effluents. The solutions required are:

(i) N/8 potassium permanganate, 3·94 gm. per litre;

(ii) N/80 potassium permanganate, prepared by dilution of the N/8 solution;

(iii) dilute sulphuric acid containing 1 volume of concentrated H_2SO_4 in 3 volumes of water and rendered

permanently pink by the addition of a few drops of the N/80 $KMnO_4$;

(iv) sodium thiosulphate solution, 6·2 gm. of $Na_2S_2O_3$. $5H_2O$, and 1 gm. of sodium carbonate per litre;

(v) starch solution.

The relative volumes of the sample and permanganate solution to be taken for the determination depend on the purity of the sample, as it is necessary that at least half of the permanganate solution shall not be reduced during the 4 hours' incubation. If the test is applied to waters of potable quality, 100 ml. of the sample and 50 ml. of the permanganate solution should be used. For good quality sewage effluents, 50 ml. of effluent and 50 ml. of permanganate should be satisfactory, but poor quality effluents and settled sewages require 50 ml. of permanganate to 25 ml. of sample, while sewages and industrial effluents should be given 100 ml. of permanganate per 25 ml. of sample. In the case of strong sewage and effluents it becomes necessary to reduce still further the proportion of sample to permanganate. Having decided on the volumes of sample and permanganate to be used, the volume of distilled water required for the total volume of the mixture (*sample + potassium permanganate + 10 ml. of sulphuric acid + distilled water*) to equal 160 ml. must be calculated; e.g. 25 ml. of sample + 50 ml. permanganate + 10 ml. H_2SO_4 will require 75 ml. of distilled water. A blank test containing 125 ml. of distilled water and 10 ml. H_2SO_4 and reacted with 25 ml. of permanganate solution must also be allowed for.

The determination is best carried out in bottles of about 250 ml. capacity and fitted with glass stoppers. Into each bottle are measured the calculated volume of distilled water and 10 ml. of sulphuric acid. The stopper is replaced and the bottle immersed in a water-bath or incubator thermostatically controlled at 80° F. Sufficient permanganate solution for all the tests is poured into a beaker and also placed in the water-bath. After about half an hour, the predetermined volume of sample is added to the bottle, the contents mixed by gentle

rotation, and the bottle replaced in the water-bath. After a further 15 minutes or so, the required volume of the now warm permanganate solution is measured into each bottle and the contents mixed. The time of incubation is measured from the moment of mixing. After 4 hours, each bottle is removed in turn from the water-bath, a few crystals of potassium iodide are added, the stopper is replaced immediately, and the bottle shaken. The excess of permanganate is thus destroyed by reaction with the potassium iodide with the liberation of iodine. The iodine is then titrated with the sodium thiosulphate solution, using the starch solution as indicator. It is essential to shake the bottle vigorously after each addition of thiosulphate solution, especially as the end-point is approached. The starch is not, of course, added until the yellow colour of the iodine has almost disappeared.

The above general procedure is not universally applicable. When the sample contains sulphides, the order of addition of the sample and permanganate should be reversed. There are other cases when this is advisable, most usually with chemical wastes containing reducing substances (e.g. sulphites) from which previous admixture with the acid would cause evolution of gas. Some very strong wastes, such as tannery waste, sulphur vat dye wastes, and gas liquors, have such high immediate reducing power that it is necessary to take only a very small volume of the sample. In some cases, series dilutions may be necessary; only oxygen-free water should be used for this if excessive oxidation of the sample during dilution is to be avoided. Freshly boiled distilled water which has been cooled without shaking must generally suffice for the purpose.

Since 1 ml. of N/80 potassium permanganate solution contains the equivalent of 0·0001 gm. of oxygen, the weight of oxygen absorbed by 100,000 parts of the sample under the conditions of the determination is given by

$$(V - 25y/x) \times 0·0001 \times 100,000/V_s$$
$$= (V - 25y/x) \times 10/V_s,$$

in which V = vol. of $KMnO_4$ solution added, y = vol. of

$Na_2S_2O_3$ solution required for the titration, $x =$ vol. of $Na_2S_2O_3$ solution required for the titration of the blank determination containing 25 ml. of $KMnO_4$, and $V_s =$ volume of sample used.

It will be appreciated that the potassium permanganate solution, which has been warmed in preparation for the test, is liable to suffer some slight concentration. This is not sufficient seriously to affect the result, but any permanganate solution which may be left unused should not be returned to the stock bottle or the slight error introduced by the evaporation will become accumulative and appreciable.

(b) Using N/8 Potassium Permanganate.

The oxygen consumed test with acid permanganate solution was formerly carried out with N/8 permanganate solution and without dilution of the mixture to 160 ml. Apart from this, there is no difference between the procedure using N/8 $KMnO_4$ and that using N/80 $KMnO_4$ except that it is often necessary to add water to the final solution to maintain the iodine in solution. As might be anticipated, there is considerable difference between the results, N/8 $KMnO_4$ giving values of the order of 1·6 times those given by N/80 $KMnO_4$. One big disadvantage of the use of the stronger permanganate solution is that the final solution of iodine is at times so concentrated that iodine is inadvertently lost by volatilization. If, therefore, it is necessary for some special purpose to employ N/8 $KMnO_4$, the test solutions should be cooled before the potassium iodide is added, and this reagent should preferably be added in good excess in the form of its saturated solution.

Determination of Oxygen absorbed from Acid Potassium Permanganate in 3 Minutes at 80° F. (26·7° C.).

This test is carried out in exactly the same way as the 4 hours' test using N/80 $KMnO_4$, but the incubation time (or reaction time) is exactly 3 minutes. The determination is of particular value in the examination of sewages and sewage effluents as the ratio (O_2 absorbed in 4 hr.)/(O_2 absorbed

in 3 min.) is generally about 3 for domestic sewage, and any big departure from this value indicates the presence of inorganic reducing substances introduced by industrial wastes. The test is also useful in helping to decide on the dilution necessary for the 4 hours' determination.

Determination of the Stability of Effluents by Incubation.

This test is applied to sewage effluents. The oxygen absorbed in 3 minutes is first determined on the fresh sample. A small bottle fitted with a ground-glass stopper is then filled completely with the sample, all air bubbles are carefully removed, and the stopper replaced. This portion of the sample is then incubated at 80° F. for 5 days, after which the oxygen absorbed in 3 minutes is again determined. If the value obtained after incubation is greater than that obtained with the fresh sample, the effluent has deteriorated and is considered unsatisfactory. If this has happened, a dark-coloured deposit may have formed on the bottom of the bottle and the incubated material may have a sulphurous or putrid odour. Exposure of the incubated sample to air very often results in the precipitation of sulphur. If the effluent is satisfactory, the oxygen absorbed from permanganate in 3 minutes will be less after incubation than it was before. The odour of the sample may improve, and no sulphur will be precipitated on standing.

Determination of Oxygen consumed from Boiling Permanganate.

This method has had an interesting history, appearing to have been first proposed by Forchammer in 1849. It has been modified and remodified many times, alternately praised and condemned. It is most widely used in America, being described in *Standard Methods for the Examination of Water and Sewage*,* whereas the 4 hours' modification of it (*vide supra*) is not. It has actually changed little in spite of the

* See footnote to p. 13.

everlasting controversy, and it is interesting to compare the description of it given in the latest edition of *Standard Methods* with that given by Wanklyn in his *Water Analysis*.* The principle of the method is that a portion of the sample is boiled with acid or alkaline potassium permanganate for a definite time, the excess permanganate is reduced by the addition of a measured excess of reducing agent, and the excess of reducing agent is then determined by titration with potassium permanganate. The reaction may be carried out in acid or in alkaline solution, or in both. The concentration of acid or alkali must be standard, as must also the time of reaction, if the results obtained by different workers are to be comparable.

The solutions required for the determination are 25 per cent by volume sulphuric acid, N/80 potassium permanganate, N/80 ammonium oxalate solution (0·888 gm. per litre), and a 33 per cent solution of sodium hydroxide. At least half of the permanganate must remain unused in the reaction, so that the volume of sample to be taken must be judged according to its purity. Generally, 10 ml. of sewage, 25 ml. of a sewage effluent or industrial water, and 100 ml. of a potable water are suitable quantities. Whatever the volume of sample used, it must be made up to 100 ml. with distilled water in a conical flask of about 250 ml. capacity. 10 ml. of the sulphuric acid or 0·5 ml. of the sodium hydroxide solution and 10 ml. of the standard potassium permanganate solution are then added and the flask is immersed in a boiling water-bath for exactly 30 minutes. 10 ml. of the standard ammonium oxalate solution are added to reduce the excess permanganate, and the solution is then titrated with the potassium permanganate solution, the end-point being marked by a faint pink colour. A blank determination must be performed with distilled water. The result is given by

{(ml. of $KMnO_4$ required for titration − ml. $KMnO_4$ required for the blank)/ml. of sample taken} × 100 = oxygen consumed in p.p.m.

* Kegan Paul, Trench, Trubner & Co. Ltd., London, 1907, p. 69.

There is little point in expressing the results in any units other than parts per million.

If the sample contains appreciable quantities of chlorides, the determination is best carried out in alkaline solution as the reaction between potassium permanganate, sulphuric acid, and chloride with the liberation of chlorine is thereby avoided.

" Oxygen Absorbed " from Sodium Hypochlorite.

This determination has a special value when it is carried out in conjunction with a similar determination with acid potassium permanganate. It is more correct to speak of it as a determination of chlorine demand, but the results obtained are different from those obtained with chlorine water. The special value lies in the fact that the ratio (oxygen absorbed from acid permanganate)/(oxygen absorbed from sodium hypochlorite) is often less than unity if the organic matter is of animal origin and greater than unity if the organic matter is of vegetable origin. This fact was discovered by Buydens,* who carried out the two determinations at boiling-point, but used widely different concentrations of the reagents. Dixon and Jenkins† also employed different concentrations of potassium permanganate and sodium hypochlorite, the reactions being allowed to proceed for ten minutes at boiling-point. Gibson‡ has found that the hypochlorite oxidation can be carried out quite satisfactorily at 80° F. and with a N/80 solution, thus making it directly comparable with the acid permanganate method which is most widely used in this country. There seems little reason to doubt that similar results would be obtained if the hypochlorite oxidation were carried out at boiling-point under conditions directly comparable with the American *Standard Method*. Gibson recommends the following procedure.

Add a suitable volume of the sample (cf. p. 43) to 50 ml. of N/80 sodium hypochlorite solution contained in a stoppered bottle and digest the mixture in a water-bath at 80° F. for 4 hours. Then add 2 ml. of a 10 per cent solution of potassium

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* *Water Poll. Res. Abs.*, 1936, 9, 51.   † *Analyst*, 1939, 64, 735.
‡ *Analyst*, 1942, 67, 125.

iodide and 10 ml. of concentrated hydrochloric acid. The excess hypochlorite—at least half of which should remain unreduced—liberates iodine from the potassium iodide and this is determined by titration with standard (N/40) sodium thiosulphate solution. A ·blank determination must be carried out at the same time. The result is given in parts per 100,000 by

$$(V -$$

in which $V = $ vol. NaOCl solution added (generally 50 ml.), $y = $ vol. of $Na_2S_2O_3$ solution required for the final titration, $x = $ vol. of $Na_2S_2O_3$ solution required for titration of the blank (containing 50 ml. of the NaOCl solution), and V_s is the volume of sample taken, in ml.

As a study of Gibson's paper will show, there is no doubt that the ratio of the " oxygen " absorbed from potassium permanganate to that absorbed from sodium hypochlorite may be of very great value in tracing a source of pollution. As stated above, the value of the ratio is

$$\frac{\text{O.A. from NaOCl}}{\text{O.A. from KMnO}_4} > 1, \text{ for animal pollution,}$$

$$\frac{\text{O.A. from NaOCl}}{\text{O.A. from KMnO}_4} < 1, \text{ for vegetable pollution.}$$

Determination of Chlorine Demand.

Although the method just described is actually a determination of chlorine demand, it is recommended in *Standard Methods* that chlorine water should be used. The results obtained with the two reagents are naturally very different, and as the determination of chlorine demand is usually carried out as a control test for chlorination purposes it is better to employ chlorine water. Several authors have recommended the determination of the chlorine demand of sewage as providing a better indication of its organic matter, and hence of the load placed on the aeration plant, than the permanganate test. Faber* has recently summarized the application

* *J. Amer. Water Works Assoc.*, 1942, **34**, 746.

of the chlorine demand test to the control of water-works operations.

A solution of chlorine is prepared by passing the gas through distilled water until a concentration of about 1 gm. per litre is reached.   The chlorine content of this solution must be checked each time it is used.   This is done by diluting 5 ml. of the chlorine water with 150 ml. of distilled water and adding an excess of crystalline potassium iodide and a few drops of concentrated hydrochloric acid.   After 5 minutes the iodine liberated is titrated with N/40 sodium thiosulphate solution, 1 ml. of which is equivalent to 0·886 mgm. of chlorine.

1·0 gm. of *o*-tolidine is dissolved by grinding it with 180 ml. of concentrated hydrochloric acid and making up to a litre with distilled water.   This solution should be stored in a brown glass bottle.

The *chlorine demand* of a sewage or polluted water is *defined* as the weight of chlorine (quoted in p.p.m.) which must be added to give a slight excess (or " residual ") after reaction for ten minutes at room temperature.   To 250 ml. of the sample in a conical flask add the chlorine water 0·5 ml. at a time from a burette, testing the mixture after each addition by withdrawing approximately 0·25 ml. in a micropipette and mixing this with a drop of the *o*-tolidine solution on a spot plate; when excess chlorine is present, a yellow colour develops in this mixture.   It is obvious that this preliminary determination must be completed within 10 minutes, and this is facilitated by using a burette with a wide orifice.   Note the volume of the chlorine water required for this titration.   To a series of conical flasks add 250 ml. of the sample and the volume of chlorine water determined by the preliminary titration (x), plus 0·25, 0·50, 0·75, 1·0, and 2·0 ml. in addition, and leave the solutions to react for exactly 10 minutes.   At the end of this time test each of the solutions for residual chlorine by decanting 100 ml. of the solution into a Nessler glass and adding 1 ml. of the *o*-tolidine solution.   A standard containing 0·1 p.p.m. of chlorine should be prepared at the same time.   After allowing 5 minutes for the development of the colour, compare the test solutions with the standard.   If

the test solution containing $x + 1$ ml. of the chlorine water has a colour less than that of the standard, whilst that containing $x + 2$ ml. is too deep ($x =$ ml. of chlorine water required for the preliminary titration), repeat the test, adding this time $x + 1.5$ and $x + 1.75$ ml. of the chlorine water. Similarly, if $x + 2$ ml. was insufficient to produce a chlorine residual of 0.1 p.p.m., repeat the test with larger quantities of chlorine water.

The chlorine demand in p.p.m. Cl is given by (ml. of Cl_2 solution required) $\times$ (concentration of chlorine water, in gm. per litre) $\times$ 4.

The Biochemical Oxygen Demand

This measurement is now recognized as the most valuable guide to water quality which has yet been devised. What is not by any means settled is the manner in which the test is to be performed. It would not be practicable in the space available to attempt to review the numerous papers which have been published on this subject, nor even to give a complete list of references to these works. In common with all empirical tests, the determination of the biochemical oxygen demand (B.O.D.) suffers from a host of variable factors, and it is unfortunate that a standard procedure has not been adopted which would assist the production of comparable results by all workers in the field of water and sewage analysis. The basis of the test is the measurement of the weight of dissolved oxygen consumed by a sample of the water during incubation for a definite period at a definite temperature. The result is calculated to parts of oxygen per 100,000 parts of sample (or to p.p.m.). The time and the temperature of incubation are now fairly standardized at 5 days at 65° F., but results are sometimes obtained in 3 days at 80° F., and occasionally, for special comparative experiments, the time is shortened still further. It follows that it is necessary to state both the time and the temperature when reporting the results.

Dilution.

It is not necessary to dilute potable waters since their B.O.D. must be very small. Less pure waters may require considerable dilution in order that the test may be applied. The solubility of oxygen in water at 65° F. is only about 10 p.p.m., and as this dissolved oxygen is the reagent by which

the organic matter is oxidized in this test, it is obvious that not only is considerable dilution necessary if the sample contains an appreciable amount of organic matter, but also that the result obtained will vary with the dilution employed. For this reason it is stipulated that at least half of the dissolved oxygen originally present in the diluted sample must remain when the test is completed after incubation for 5 days. The dilution necessary for samples of approximately known B.O.D. can be calculated. Basing the calculation on a standard diluted volume of 1 litre, the total weight of oxygen available for the measurement is approximately 0·01 gm. if the diluted solution is initially saturated with dissolved oxygen. In order that 0·005 gm. of oxygen shall remain after incubation for 5 days, waters with a B.O.D. value not greater than 0·5 part per 100,000 need not be diluted at all. Similarly,

B.O.D. of sample. (parts per 100,000)			Volume of sample to be diluted to 1 litre.	
0·5	to	5	100	ml.
5	to	25	20	ml.
25	to	50	10	ml.
50	to	100	5	ml.
100	to	500	1	ml.
500	to	1000	0·5	ml.
1000	to	5000	0·1	ml.

When the B.O.D. is so high that it becomes necessary to take less than 5 ml. of the sample for the dilution, series dilutions are advisable, that is to say, first dilute, say, 10 ml. of the sample to 100 ml. with distilled water, then dilute an aliquot of this solution. There is practically no limit to the B.O.D. values which may be found with certain trade effluents.

Dilution Water.

There is much difference of opinion as to the water to be used for dilution of the sample. The original proposal for sewage effluents was to use water from the stream into which an effluent was to flow, but although this is probably the best way to assess the effect of an effluent on a stream, the result

when obtained is characteristic of one effluent and one stream, and is not comparable with any other result obtained elsewhere. It is also quite impossible to apply this principle in a central laboratory which may have to examine effluents from numerous sources entering an equal number of streams. The use of distilled water as diluent was soon found to be unsatisfactory, as distilled water does not support bacterial life; incidentally it is for this reason that distilled water is recommended for use in serial dilutions. Several authors have studied in detail the problem of dilution water and have recommended the addition to distilled water of traces of mineral salts, more particularly phosphates. However, as is illustrated by a recent review by Buswell and Dunlop,* the matter is still far from settled.

The most usual dilution water to employ in this country is plain tap water which has been well shaken and stored at 65° F. for some little time before use. Since the general quality of water supplies in this country is so good, there is less objection to their use for this purpose than there might be in the United States, where water supplies are frequently obtained from rivers and lakes which receive the sewage of neighbouring towns. This statement is not meant to imply any criticism of American water supplies, which generally receive rigorous scientific purification, but only to show that these same treatments are liable to render the resultant tap-waters less comparable one with another than those which are supplied in Britain.

Determination of B.O.D. by the Alkaline Azide Method.

This modification of the Winkler method was employed successfully by the author for the examination of sewages and effluents. According to Thompson,† it was first proposed by Dr. Kessener of the Hague, although others have laid claim to it since. The solutions required are:

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* *J. Amer. Water Works Assoc.*, 1942, **34**, 1063.
† *Ann. Conf. Public Works, Roads, and Transport Services*, 1933, No. 24.

(1) Sodium hydroxide 330 gm., potassium iodide 200 gm., sodium azide 5 gm., dissolved in 1 litre of distilled water.

(2) 400 gm. of crystalline manganous chloride in 1 litre of water.

(3) Concentrated phosphoric acid, sp. gr. 1·27.

A suitable volume of the sample is diluted to 1 litre with tap-water which has been shaken with air and stored at a temperature of about 65° F. for several hours.   Two 10-oz. bottles fitted with ground-glass stoppers are filled completely with the diluted sample, the solution being poured into the bottles gently and without splashing.   Any small bubbles of air which may lodge under the shoulder of a bottle must be removed by tapping the glass.   3 ml. of the alkaline iodide solution (1) are measured in a graduated 5-ml. pipette and then added to one of the bottles, holding the orifice of the pipette well down the neck of the bottle under the surface of the solution.   The heavier alkaline iodide solution sinks to the bottom of the bottle and a corresponding volume of the diluted sample is displaced and allowed to flow to waste.   3 ml. of the manganese chloride solution are then added in the same way. The stopper of each bottle is replaced carefully, making sure that no bubbles of air are trapped beneath the stopper.   The untreated bottle is placed in the incubator at 65° F.   The contents of the other bottle are mixed thoroughly by vigorous rotation, after which it is set aside for 1 hour.   6 ml. of the concentrated phosphoric acid are then added, running the liquid below the surface as before, the stopper is replaced, and the bottle again shaken.   An amount of iodine equivalent to the dissolved oxygen originally present in the diluted sample is liberated at this stage.   Any nitrites which may have been present react with the sodium azide with the production of nitrogen. 100 ml. of the solution are measured and titrated against N/40 sodium thiosulphate, using starch indicator.

After 5 days, the second bottle of diluted sample is removed from the incubator, the reagents are added in exactly the same way, and a 100-ml. portion is titrated with standard thiosul-

phate solution. The calculation of the result is best illustrated by means of an example.

Example.

10 ml. of a sewage were diluted to 1 litre with aerated tap-water. After treatment as described above, 100 ml. of the iodine solution required 4·8 ml. of $N/40$ thiosulphate solution. After incubation, 100 ml. of the iodine solution produced by the reaction with manganous chloride and potassium iodide oxidized 3·5 ml. of the thiosulphate solution. 1 ml. of $N/40$ sodium thiosulphate solution will oxidize iodine equivalent to $8 \times 1/40 \times 10^{-3}$ gm. of oxygen, i.e. 2×10^{-4} gm. of oxygen. Consequently, the initial solution contained $4·8 \times 2 \times 10^{-4}$ gm. of oxygen in 100 ml., whilst the solution after incubation contained $3·5 \times 2 \times 10^{-4}$ gm. of oxygen per 100 ml. The difference, i.e. $1·3 \times 2 \times 10^{-4} = 2·6 \times 10^{-4}$ gm. of oxygen was consumed by the volume of effluent contained in 100 ml. of the diluted sample; this volume was 1 ml. The weight of oxygen consumed by 100,000 ml. of sewage was therefore $2·6 \times 10^{-4} \times 10^{5} = 26·0$. This is the B.O.D. of the sample.* A blank determination should be run on the dilution water and subtracted from the oxygen consumed by the sample.

Many modifications of the determination have been proposed. The object of most of these variations has been the elimination of the interference of nitrites in the determination of the dissolved oxygen. The azide method, of course, is only one of these modifications. The only reason for including it in preference to the many others is that the author happens to have used it for many hundreds of determinations and has found it convenient and satisfactory.

The Rideal and Stewart Modification of the Winkler Method.

The Winkler method as modified by Rideal and Stewart is that recommended by the Ministry of Health and is probably most widely used in this country. The concentrations of the

* For the procedure to be adopted with strong sewages and trade wastes, see p. 58.

reagents are slightly different from those given above, and the nitrites are destroyed by the addition of acid and potassium permanganate. The latter reagent, which would itself interfere with the determination, is reduced by the addition of sodium oxalate.

The solutions required are:

   (i) N/8 potassium permanganate.
  (ii) A 2 per cent solution of potassium oxalate.
 (iii) Manganous chloride solution, 33 per cent.
 (iv) Alkaline potassium iodide solution, 70 per cent KOH
       and 10 per cent KI.
  (v) Standard sodium thiosulphate solution.

The dilution of the sample is carried out as described above and two bottles are filled with the dilute solution. One of these is placed in the incubator for 5 days at 65° F. The dissolved oxygen is determined immediately in the other. 0·9 ml. of concentrated sulphuric acid is added, followed by 1 or 2 ml. of the potassium permanganate solution, and the stopper of the bottle is inserted. The contents are mixed by vigorous rotation of the bottle, which is then set aside for 20 minutes. This is the period recommended for the destruction of nitrites. The solution should be distinctly pink at the end of this time. The excess permanganate is then reduced by the addition of 1 ml. of the potassium oxalate solution, the stopper is immediately replaced and the contents mixed. When the solution is colourless, 1 ml. of manganous chloride solution is added, being run in below the surface of the liquid, and this is followed immediately by 4 ml. of alkaline iodide solution, delivered beneath the surface of the liquid from a pipette with a wide orifice. The stopper is replaced immediately and the bottle rotated. After standing for several minutes—until the precipitate has settled about half-way down the bottle—the bottle is again rotated and left to stand until the precipitate has settled. 5 ml. of concentrated hydrochloric acid are then added, the contents mixed, and after a further 5 minutes the iodine liberated may be determined by titration with the standard thiosulphate solution as described in the previous

section. The result is obtained in the same way as was illustrated previously.

A comparison of this procedure with the alkaline azide method will show that it involves more additions to the contents of the bottle and several additional removals of the stopper. This increases the risk of absorption of atmospheric oxygen, but it also entails some practical difficulty. In fact, it is difficult to replace the stopper of the bottle without trapping bubbles of air unless the bottle is full to the brim. This is certainly not the case when the potassium oxalate has been added.

The B.O.D. of Strong Sewages and Trade Effluents.

Sewages containing trade effluents often contain chemical substances which reduce dissolved oxygen immediately on mixing with the dilution water. In order that this immediate effect may be taken into account, it is necessary to calculate the amount of dissolved oxygen present in the original mixture before incubation. This may be done on the assumption that the sewage itself contains no dissolved oxygen. The concentration present in the dilution water is already known from the blank. Consequently, the concentration of dissolved oxygen in the mixture of sewage and dilution water is given by

$$\frac{(\text{concn. in dilution water}) \times (\text{vol. of dilution water used})}{(\text{total vol. of dilution water and sample})}.$$

The " immediate " B.O.D. is sometimes measured; it is carried out in the same way as the ordinary determination, except that the initial oxygen concentration is calculated and the dissolved oxygen remaining 15 minutes after mixing is measured. The immediate B.O.D. is therefore in reality the 15-minute B.O.D.

Dissolved Oxygen.

The measurement of the oxygen dissolved in water is of particular importance. Sewage usually contains very little dissolved oxygen owing to the fact that it is used up by the

organisms present in the sewage as fast as it can dissolve from the air with which the sewage is in contact in the sewer or conduit. As has been stated, the rate at which a water consumes dissolved oxygen, which is measured as the biochemical oxygen demand, is an excellent measure of its degree of pollution. It follows that, provided that there is ample contact between the water and the air, the more dissolved oxygen the water contains, the greater is its purity. A cold, pure, mountain stream flowing rapidly in a rocky bed may be expected to be saturated with dissolved oxygen, as the conditions are then ideal for the dissolution of air in the water. The concentration of dissolved oxygen varies directly with the purity of the water, and the opportunity for the dissolution of air, and inversely with the temperature.

The presence of dissolved oxygen in boiler-feed water is not desirable owing to its accelerating effect on the corrosion of iron.

Determination of Dissolved Oxygen.

The determination is carried out exactly as described under Biochemical Oxygen Demand but without dilution of the sample. It is essential that the sample should be fresh and that it should be contained in a completely filled bottle. It is always preferable to take a special sample for the purpose, filling the bottle completely by holding it beneath the surface of the water. A sampling bottle of the type in fig. 4 (p. 60) is suitable for the purpose, since it can be used to take samples from any desired depth and there is the minimum of contact between the water entering the bottle and the air leaving it.

The alkaline azide method for dissolved oxygen determination (see p. 54) is convenient for use in the field; the manganous chloride and the alkaline iodide solutions can be added to the sample immediately it has been taken and, after mixing, the rest of the determination can be carried out on returning to the laboratory.

Circumstances usually dictate the manner in which samples shall be taken. Bearing this fact in mind, detailed directions are superfluous and it must suffice to stress that the sample

bottle should be filled completely with the sample in such a way as to minimize contact between the liquid and air, and thereafter the determination should be completed as soon as
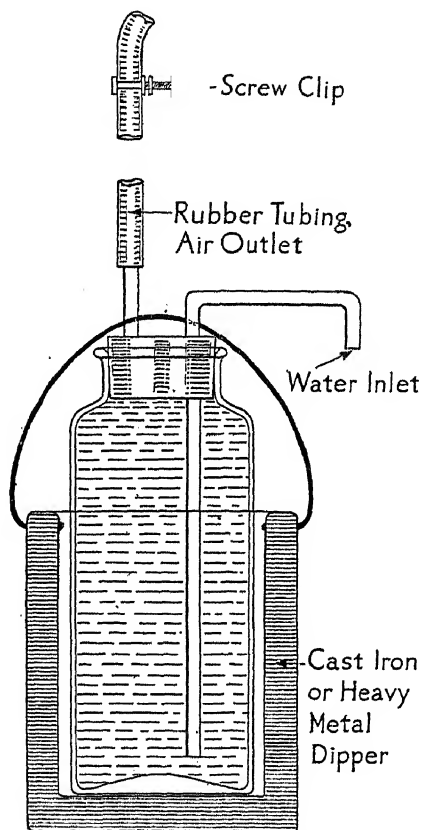

Fig. 4.—Sampling bottle

possible. Increasing the temperature of the sample in transit must be avoided at all costs.

An alternative method for the determination of dissolved oxygen which has been recommended for field use is as follows.

Determination of Dissolved Oxygen by the Miller Method.

Originally described by Miller,[*] a slightly modified method was quoted by Thompson.[†] The solutions required are:

(i) Alkaline tartrate solution, containing 350 gm. Rochelle salt and 100 gm. sodium hydroxide in a litre of distilled water;

(ii) Ferrous ammonium sulphate, stock solution, containing 10·75 gm. of the salt and 10 ml. of concentrated (98 per cent) sulphuric acid per litre of water.

(iii) Ferrous ammonium sulphate, dilute solution, prepared by diluting 50 ml. of (ii) to 100 ml.; this solution should be prepared and standardized as required. As the method is to some extent empirical, this solution must be standardized against a water containing a known concentration of dissolved oxygen. It is generally most convenient to saturate tap-water with air by frequent shaking in a bottle, and to determine its oxygen content by one of the Winkler methods already described. The same water can then be used for the standardization of the ferrous ammonium sulphate solution. Alternatively, if the appropriate solubility tables are available, the dissolved oxygen concentration in the water may be calculated.

(iv) Indicator solution containing 1·0 gm. of methylene-blue per litre of water.

(v) Pure paraffin oil.

Allow the sample to settle and decant 50 ml. of the clear supernatant liquid into a 100-ml. Nessler glass. Add 3 ml. of paraffin oil to protect the surface from contact with the air and two drops of the indicator solution. Run 5 ml. of the alkaline tartrate solution down the side of the tube into the liquid. Titrate with the standard ferrous ammonium sulphate solution, using a 10-ml. burette fitted with a long delivery tube

[*] *J. S. C. I.*, 1914, **33**, 185.
[†] *Public Works, Roads, and Transport Congress*, 1933, No. 24.

so that the tip dips into the solution being titrated. Gentle stirring should be effected with a glass plunger or a slow stream of nitrogen. The end-point is marked by the disappearance of the blue colour.

The result is given by

$$(\text{ml. ferrous ammonium sulphate required}) \times 2\cdot5$$
$$= \text{p.p.m. dissolved oxygen.}$$

Sulphites and nitrites do not interfere with the method. If much ferric iron is present, add 3 ml. of 40 per cent potassium fluoride solution before commencing the titration.

This method is not as accurate as the Winkler methods unless the dissolved oxygen concentration is fairly high, say greater than 2·5 p.p.m. However, it is useful for field and control tests as the result is available in a very short time.

Nitrites and Nitrates

The presence of nitrates in a stream is not unusual as they are natural products of bacterial oxidation, but any considerable amount would be regarded as suspicious, especially if nitrites were also present. Fairly large amounts of nitrites are found in the drainage waters from agricultural land and refuse dumps. They are present in sewage in wet weather and are nearly always found in the effluents from activated sludge treatment plants. Nitrates are highest in the effluents from nitrifying filters and are seldom present in any quantity in effluents from activated sludge plants.

There are several colorimetric methods available for the determination of nitrites. The Griess-Ilosva method has been selected for description as it is more sensitive than most, and also because the colour produced is red and is therefore more easy to measure than yellow or brown. As a preliminary test the well-known reaction with acid starch-iodide may be employed provided that free chlorine is not suspected.

Preliminary Test for Nitrites.

To 50 ml. of the sample in a Nessler glass add 1 ml. of saturated potassium iodide solution, 3 or 4 drops of starch solution, and 1 ml. of concentrated hydrochloric acid. The nitrites liberate iodine, which gives a blue colour with the starch. The time taken for the development of the colour will be found to be a fairly reliable guide to the nitrite content, and with experience this preliminary test will assist in the choice of standards for the more precise determination.

Griess-Ilosva Method for Nitrites.

The sample is first decolorized if necessary by a suspension of alumina. This is prepared by the addition of aqueous

ammonia to a solution of 125 gm. of potassium alum in a litre of distilled water, the precipitate being filtered off and freed from ammonia by repeated suspension in fresh distilled water. It should be free from nitrites and nitrates. The alumina is finally suspended in a litre of distilled water.

Other solutions required are:

Sulphanilic Acid. 8 gm. of pure sulphanilic acid are dissolved in 1 litre of 5 N acetic acid.

α-Naphthylamine. 5 gm. of α-naphthylamine are dissolved in 1 litre of 5 N acetic acid and the solution filtered through cotton wool.

(*Note.*—Both the above solutions are difficult to prepare, as they are nearly saturated.)

Sodium Nitrite Solution A. 1·10 gm. of silver nitrite is dissolved in distilled water, the calculated quantity of pure sodium chloride, dissolved in a little water, is added to precipitate the silver, and the silver chloride is filtered off. The filtrate is diluted to 1 litre.

Sodium Nitrite Solution B. 100 ml. of the solution A are diluted to 1 litre. 50 ml. of the resultant solution are diluted to 1 litre, 1 ml. of pure chloroform is added and the solution is bottled and stored in the dark. 1 ml. of this solution contains 5×10^{-7} gm. of nitrous N.

100 ml. of the sample are shaken with 1 ml. of the suspension of alumina, allowed to settle and then filtered through a dry paper. After rejecting the first 20 ml. of filtrate, 50 ml. are collected in a Nessler glass. 25 ml. of the filtrate are collected in a second Nessler glass, followed by distilled water to the 50-ml. mark. To a series of identical Nessler tubes are added measured volumes of the sodium nitrite solution B, say, 0·3, 0·6, 1·0, 1·4, 1·8, and 2·2 ml., and the volume made up to 50 ml. in each case with distilled water. Equal volumes of the sulphanilic acid and α-naphthylamine solutions are mixed and 2 ml. of the mixed solution are added to each sample and to each standard. The contents of the tubes are then mixed with a glass rod and allowed to stand for 10 minutes for the red colour to develop. The colours of the samples are then compared with the standards. If neither sample has a colour

comparable with that of any of the standards, the test should be repeated, using either a more diluted sample or a fresh set of standards. If the colour produced by 25 ml. of the sample is too deep, it is useful to dilute it progressively until a colour is obtained which falls within the range of the standards; this will provide a guide to the dilution required before repeating the determination.

Preliminary Test for Nitrate in the Presence of Nitrite.

Take 25 ml. of the sample, filtered if necessary, and evaporate to dryness over a bunsen burner. Add 5 ml. of concentrated sulphuric acid and a trace of solid brucine. If nitrate is present, a red colour is produced and changes gradually to yellow.

Colorimetric Determination of Nitrate.

Of the many methods which are available for the determination of nitrates in waters the phenoldisulphonic acid method of Sprengel is that most commonly employed.

Determination of Nitrates by the Phenoldisulphonic Acid Method.

This method is accepted as a standard method for nitrates in water and sewage. It is subject to interference from chlorides, nitrites, and carbohydrates. The modification described below removes the chlorides, but if nitrite is present in excess of 1 p.p.m. a portion of the sample must be acidified with a drop of concentrated hydrochloric acid and warmed for a few minutes with a few drops of hydrogen peroxide. This oxidizes the nitrite to nitrate, and the extra nitrate thus produced must be corrected for by calculation from the concentration of nitrite found to be present in the sample. The solutions required are:

(i) *Phenoldisulphonic Acid.* Melt 18 gm. of pure white phenol with 9 ml. of distilled water in a flask and add 111 ml. of reagent quality concentrated sulphuric acid. Digest the mixture on a water-bath for 8 hours. Alternatively, since phenoldisulphonic acid can be

purchased in a pure state, a sulphuric acid solution of equivalent concentration may be prepared.

(ii) *Sodium Hydroxide Solution*, approximately 50 per cent.

(iii) *Standard Potassium Nitrate Solution.* Dissolve 0·7216 gm. of the pure dry salt in a litre of water.

(iv) *Standard Silver Sulphate Solution*, containing 4·397 gm. per litre. 1 ml. of this solution is equivalent to 1 mgm. Cl.

Prepare a standard solution by evaporating 50 ml. of the standard nitrate solution to dryness on a water-bath. Moisten the residue quickly with 2 ml. of the phenoldisulphonic acid and rub the mixture with a glass rod. Wash the solution into a 500 ml. graduated flask and make up to the mark with distilled water. 1 ml. of this solution contains the equivalent of 0·01 mgm. of nitric nitrogen.

To an appropriate volume of the sample, 10 ml. of an effluent from nitrifying filters, 25 ml. of other sewage effluents, or 100 ml. of potable water, add sufficient standard silver sulphate solution to precipitate all the chloride in excess of 10 p.p.m.. If the sample is decidedly alkaline, it must be neutralized before adding the silver sulphate. An excess of silver sulphate should be avoided. Filter the solution into an evaporating basin and evaporate to dryness on a water-bath. As soon as the residue is dry, add 2 ml. of the phenol-disulphonic acid, rub with a glass rod, and add the sodium hydroxide solution until the maximum yellow colour develops. Filter if necessary through an alkali-resistant paper into a 50-ml. Nessler glass.

Into a series of similar Nessler glasses measure 0·1, 0·3, 0·5, 0·7, 1·0, 3·5, 7·0, and 10·0 ml. of the standard solution and add to each 2 ml. of the sodium hydroxide solution. Make all the solutions to 50 ml. with distilled water and compare the unknown with the standards. The standard colours are reasonably stable if kept in the dark.

The result is given by

$$\frac{\text{(mg. of N in the matched standard)}}{\text{(ml. sample taken)}} \times 10^3 = \text{p.p.m. N.}$$

Determination of Nitrates with Brucine.

The author recommends the method described by Gad.*

1 ml. of the filtered sample is added to 10 ml. of 64 per cent (by volume) sulphuric acid. 0·1 ml. of a solution containing 5 gm. of brucine in 100 ml. of acetic acid is added, followed by one drop of concentrated hydrochloric acid. The mixture is heated in a boiling water-bath for ten minutes for the yellow colour to develop. Standards are prepared from measured small volumes of a solution of pure potassium nitrate, or preferably from 1 ml. each of a series of standard dilutions of a stock solution. It is convenient to have a number of test-tubes of equal size to contain the standards and also the sample. These can be placed in a basket (of the bacteriological type) and all can be immersed in the water-bath at the same time. The colour developed by the sample is compared with those of the standards by looking down the tubes when held over a white plate. A suitable standard solution of potassium nitrate contains 0·7216 gm. per litre, when 1 ml. contains 0·1 mgm. nitric nitrogen; this is the stock solution and requires further dilution (from 100 to 200 times) before use for the preparation of standards.

Total Nitrites and Nitrates by Reduction.

It is advisable to confirm the separate results obtained for nitrites and nitrates by the above methods by a determination of the sum of the two. For routine purposes, this is not necessary, unless it is desired to check an unusual value.

The official method was devised by Ormandy and Cohen † and modified by Scudder.‡ It involves the rapid reduction of the nitrites and nitrates to ammonia in acid solution, followed by determination of the ammonia. An aluminium-mercury couple is employed for the reduction.

A portion of the sample is filtered through a dry paper and 10 or 20 ml. measured into a conical flask of 250-ml. capacity. 75 ml. of water and 0.5 ml. of N sodium carbonate solution are

* *Water Poll. Res., Abs.*, 1939, **12**, 1443.   † *J. C. S.*, 1890, 811.
‡ *Interim Report, Roy. Comm. Sewage Disposal*, Vol. II, p. 332.

added and the solution evaporated gently to about 25 ml. to drive off the ammonia naturally present. While this is taking place it is convenient to prepare the aluminium-mercury couple. A strip of pure aluminium foil, 5 cm. × 2·5 cm., is amalgamated by immersion in 1 per cent mercuric chloride solution for several minutes, after which it is washed in distilled water. It must not then be left exposed to the air or vigorous oxidation of the aluminium will take place. If it is necessary to keep it for any length of time before use it should be immersed in distilled water. When the mixture containing the sample is ready for use, the amalgamated aluminium foil is removed as rapidly as possible to a 100-ml. Nessler glass, or a boiling-tube of similar size, and the contents of the flask washed in so as to give a total volume of solution and washings of about 70 ml. 5 ml. of 25 per cent hydrochloric acid (1 vol. conc. acid to 3 vols. water) are then added, and the tube covered with a watch-glass. Rapid evolution of hydrogen will be observed and the reduction should be allowed to continue for a minimum period of 2 hours. The excess acid is then neutralized by the careful addition of sodium carbonate solution, and the contents of the tube, not forgetting any spray that may have been caught on the watch-glass, washed into a distillation flask. A convenient volume of ammonia-free water is added and the ammonia is distilled off. 200 ml. of the distillate are collected and the ammonia is determined by Nesslerization (cf. p. 39).

Normally the apparatus for ammonia distillation will be a permanent assembly, and it is then most convenient to free the apparatus from ammonia in the usual way, allow the flask to cool, and add the reduced sample to the ammonia-free water thus obtained. The apparatus may be rendered ammonia-free during the course of the reduction of the sample. Although the mixture to be distilled contains a considerable quantity of aluminium hydroxide in suspension it gives no trouble during distillation, boiling quite smoothly, but with some tendency to froth.

Heavy Metals

ZINC

The determination of zinc is normally carried out only on potable water supplies, where its presence is due to the use of galvanized storage tanks. The method generally favoured in this country is the measurement of the turbidity produced with potassium ferrocyanide in hydrochloric acid solution.

25 ml. of the sample are pipetted into a 50-ml. Nessler glass and acidified with 0·5 ml. of concentrated hydrochloric acid. 20 ml. of 10 per cent ammonium chloride solution are added, followed by a drop of sodium sulphite solution to reduce any iron which may be present to the ferrous state. While this reduction is taking place, it is convenient to prepare standards from a solution containing 0·044 gm. of crystalline zinc sulphate ($ZnSO_4.7H_2O$) per litre. 1 ml. of this solution contains 0·00001 gm. of zinc and the standards may conveniently cover the range 0 to 4 p.p.m., i.e. 0 to 10 ml. of this solution. (If 1 ml. of this solution containing 1×10^{-5} gm. Zn were found to match the unknown, the sample would contain $1/25 \times 10^{-5} \times 10^6$ p.p.m. $= 0·4$ p.p.m.) It is not permissible to use more than 10 ml. of this solution in preparing a standard. To each standard are added 0·5 ml. of concentrated hydrochloric acid, 20 ml. of 10 per cent ammonium chloride solution, and sufficient distilled water to make up to 50 ml. To each tube is now added 1 ml. of a 0·5 per cent solution of potassium ferrocyanide. The contents of each tube are stirred with a glass plunger, and the turbidity of the unknown is matched with the standards, holding the tubes over a black paper. If the turbidity produced by the

sample is greater than that of the highest standard, the test must be repeated, using a smaller volume of the sample.

COPPER

The presence of copper in potable waters may arise from the occasional treatment of reservoirs and storage tanks with small concentrations of copper sulphate to destroy algal growths. The very small concentration of copper which may thus enter the water supply is hardly significant from a public health point of view, but it may be inimical to certain industrial processes. A second source of copper is the use of copper boilers, piping, and cylinders in domestic hot-water systems. This latter source was investigated by Wilkinson and Wilson [*] in New Zealand, who found that new copper equipment gave rise to the highest copper concentration in the water and that the concentration decreased as the age of the installation increased. In no case did the amount of copper present in the water circulating in the hot-water system rise as high as 1·0 part per million. The temporary hardness of the waters in use lay between 20 and 115 p.p.m., and they were considered to be aggressive. Cylinders which had been in use for a year or more seldom gave rise to a copper concentration greater than 0·5 p.p.m. No harmful effects are likely to arise from the consumption of water containing up to 1 p.p.m. of copper, but traces of copper catalyse the oxidation of vitamin C during cooking and are therefore especially undesirable in the canning industry.[†] Copper in excess of 0·5 p.p.m. may cause unsightly staining of porcelain and enamelled baths and sinks. Such stains are easily removed by swabbing with hydrochloric acid.[‡]

Colorimetric Determination of Copper.

The most sensitive and also the most popular reagent for the determination of small quantities of copper is sodium

[*] *Analyst*, 1941, **66**, 322.
[†] Cf. Mack and Kertesz, *Food Research*, 1936, **1**, 377.
[‡] Thompson, *J. Roy. San. Inst.*, 1939, **60**, 25.

diethyldithiocarbamate. A 0·1 per cent solution of this substance in water is required; it must be stored in a brown glass bottle, preferably in the dark. 50 ml. of the sample are rendered alkaline by the addition of 5 ml. of dilute ammonia (1 volume of 0·880 ammonia in 5 volumes of distilled water), and filtered to remove any iron which may be precipitated. The filtrate is collected in a 100-ml. Nessler glass and 5 ml. of the carbamate solution are added. The volume is then made up to 100 ml. with distilled water. To a similar Nessler tube are added 5 ml. of the dilute ammonia, 5 ml. of the reagent solution, and distilled water to make up to volume. A solution of copper sulphate containing 0·01 mgm. of copper per ml. (0·0393 gm. copper sulphate, $CuSO_4.5H_2O$, per litre) is added to the standard solution from a 10-ml. burette until the colours developed in both tubes appear the same. The matching is then repeated rapidly by preparing a fresh standard containing 5 ml. of the reagent solution, 5 ml. of the dilute ammonia, nearly sufficient of the standard copper solution to match the unknown, and distilled water to make up to 100 ml. The comparison is then completed by the careful addition of more standard copper solution.

Zinc and lead interfere with the determination by producing a white turbidity. If this should be the case, the colour is extracted by shaking the solution with successive 5 ml. portions of carbon tetrachloride until no more of the colour is extracted. It is then necessary to prepare a series of colour standards from the copper sulphate solution and extract the colour of each of these with the same volume of carbon tetrachloride as was used for the test solution. Comparison of the unknown with the standards in the usual manner must then suffice.

If it is found that the volume of water taken for the determination contains more than 0·1 mgm. of copper, the determination should be repeated on a smaller volume of the sample. This is because the colour produced by quantities of copper greater than 0·1 mgm. per 100 ml. is too dark for accurate comparison with a standard. The colour is yellowish brown.

Since the standard copper solution contains 0·01 mgm. Cu per ml., the result in p.p.m is 20 × volume of $CuSO_4$ solution required × ·01 when 50 ml. of the sample are taken for comparison.*

LEAD

All drinking water which passes through lead service pipes may be expected to contain more or less lead. The factors which control the dissolution of lead in water appear not to be known with any certainty, although a great amount of work has been done on the subject. It is therefore of importance that domestic water supplies should be tested regularly for lead, especially if there has been any change in the method of treatment of the supply. There is quite a wide choice of methods for the determination of lead, all of them complicated and lengthy. The method described is somewhat shorter than most, and is based on that described by Moor and Partridge.†

Determination of Lead in the Presence of Organic Matter.

The volume of sample to be taken for the determination must depend on the amount of lead likely to be present. If there is no indication of this it may be an advantage to carry out several determinations in parallel, starting with different volumes of the sample, e.g. 5 ml., 10 ml., and 20 ml., instead of the more usual duplicate analyses. The sample is measured into a hard glass Kjeldahl flask and acidified with 5 ml. of concentrated sulphuric acid. 20 ml. of concentrated nitric acid are added and the mixture is boiled gently over a bunsen flame; it is advisable to have a glass bead in the flask to guard against bumping. The water boils off and then nitric acid fumes appear, finally giving place to white fumes of sulphuric acid. The solution should now be perfectly clear and colour-

* The literature on this determination is rather voluminous; for a bibliography of the subject see *Organic Reagents for Metals*, 3rd Edn., 1938, p. 122, Hopkin & Williams, London; for the original of the method described above see Haddock and Evers, *Analyst*, 1932, **57**, 495.

† *Analysis of Food and Drugs*, 5th Edn., revised by J. R.Nicholls (Baillière, Tindall & Cox, 1934), p. 242.

less, but if it is brown, or shows even the least sign of char-ring, a further portion of nitric acid must be added and boiled off in the same way. This process must be repeated until the residual solution is colourless. 50 ml. of distilled water are then added, and the solution is again boiled down until white fumes appear. The solution is next diluted to about 250 ml. with distilled water—it is convenient to transfer it to a 750-ml. conical flask at this stage—and 5 ml. of a 10 per cent solution of citric acid are added. A few drops of methyl-orange solution are added to colour the solution, which is then neutralized carefully by the addition first of strong ammonia, and then of diluted ammonia. It is essential that the solution after this treatment should have a p_H of about 5 (i.e. just alkaline to methyl orange). Hydrogen sulphide is now passed through the solution for at least an hour, the flask being stirred at frequent intervals meanwhile, and the precipitate is allowed to settle. The liquid is filtered through an acid-washed filter paper and the precipitate is washed with hydrogen sulphide water. After draining, the paper is folded and returned to the Kjeldahl flask, the flask in which the precipitation was carried out is washed with a little concentrated nitric acid, and these washings are added to the Kjeldahl flask. Finally, 1 ml. of concentrated sulphuric acid is added to the mixture, which is boiled until the sulphuric acid begins to fume. This wet oxidation process is merely a repetition of the initial prepara-tion of the solution and should be carried out in exactly the same way until a colourless fuming solution is obtained. 20 ml. of water are added and the solution is again evaporated until white fumes appear, when it is allowed to cool. 15 ml. of 30 per cent aqueous alcohol are added, mixed thoroughly, and the mixture left to stand overnight. A white precipitate of lead sulphate may now appear, but if the original sample contained very little lead, the amount of precipitate may be so small as to be almost invisible. However, whether the lead sulphate is visible or not, the solution is filtered through a 9-cm. acid-washed filter paper, and the flask is rinsed several times with a solution containing alcohol, water, and concen-trated sulphuric acid in the proportions 10, 20, and 1 by

volume, respectively. These washings are, of course, passed through the filter paper. 10 ml. of a 10 per cent ammonium acetate solution are now boiled in the Kjeldahl flask and passed through the filter paper, collecting the filtrate in a fresh receiver. The filtrate is returned to the flask, boiled again, and again passed through the paper. The flask and filter paper are finally washed three times with a hot dilute solution of ammonium acetate, using about 5 ml. of the solution each time. The mixed filtrate and washings are now made up to a suitable volume in a standard flask. 25 ml. of this solution are measured into a 100-ml. Nessler tube (graduated also with a 50-ml. mark). To a similar tube are added 10 ml. of the 10 per cent ammonium acetate solution. 1·5 ml. of 0·880 ammonia is added to each tube, followed by 1·0 ml. of 10 per cent potassium cyanide solution, and sufficient distilled water to make up to the 50-ml. mark. 0·1 ml. of a 10 per cent solution of sodium sulphide is then added to each tube; this solution must be freshly made. A brown colour develops in the tube containing the extracted lead. A standard lead solution containing 0·00001 gm. of lead per ml. is now added drop-wise from a 10-ml. burette to the lead-free solution until the colour matches that produced by the lead in the extract. The volume of standard lead solution required to effect this is then read, and the matching is repeated, this time adding a volume of the standard lead solution slightly less than that required for perfect matching to the standard, or control, tube and then completing the titration more cautiously. It is necessary to hold the unknown alternately on the left and right of the control tube in order to decide on the exact end-point.

The standard lead solution should be prepared from pure lead foil, dissolved in pure redistilled nitric acid and neutralized carefully. A stock solution containing 1·0 gm. of lead per litre will require dilution 1 : 100.

Owing to the inevitable presence of traces of lead in the reagents used for the analysis, it is necessary to carry a blank determination through all the stages. All additions, especially of acids, which are made to the sample must also be made to

the blank; it is therefore necessary to measure (in a cylinder) the nitric acid used in oxidizing the organic matter.

The amount of lead found in the blank is deducted from that found in the sample extract before calculating the lead content of the sample.

The above method is of fairly general application, but must be modified if there is much calcium phosphate in the sample. For such modifications see *Lead in Food*, G. W. Monier-Williams, H.M. Stationery Office, 1938, and Moor and Partridge, loc. cit.

Direct Determination of Lead in the Absence of Organic Matter.

To 50 ml. of the sample add a few drops of glacial acetic acid and filter if necessary. Add 1·5 ml. of 0·880 ammonia to the filtrate and make up to 100 ml. Measure 50 ml. of this solution into a 100-ml. Nessler glass and add 10 ml. of 10 per cent ammonium acetate solution and 1·0 ml. of 10 per cent potassium cyanide solution. To a similar tube add 50 ml. of distilled water, 1·5 ml. of 0·880 ammonia, 10 ml. of 10 per cent ammonium acetate solution and 1·0 ml. of 10 per cent potassium cyanide solution. Add 0·1 ml. of freshly prepared sodium sulphide solution to each tube. Match the colour of the unknown by adding standard lead solution to the control from a 10-ml. burette as described in the previous section.
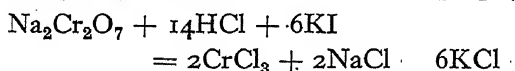
CHROMIUM

The presence of chromium in sewages arises from the discharge from industrial premises of the wash-waters used in chromium plating and, less frequently, of the spent plating baths. In view of the serious consequences which may result from the action of chromium on a sewage purification plant, a reasonably accurate method for the determination of the element in the sewage is required. Several methods have been proposed, and as it is as yet too early to decide which is the most reliable, each has been abstracted.

Spencer's Method for Total Chromium.

Spencer * recommends the following procedure for the determination of total chromium in the presence of sewage.

50 or 100 ml. of the sewage are boiled with a slight excess of alkaline potassium permanganate for several minutes. A few ml. of ethyl alcohol are then added and the mixture again boiled. The alcohol reduces the excess permanganate to manganic hydroxide, which is precipitated, and the excess of alcohol is boiled off. The liquid, which contains all the chromium in the form of chromate, is filtered into a standard flask, the precipitate washed well with water, and the total filtrate cooled and made up to 250 ml. An aliquot portion is taken and acidified with 5 ml. of concentrated hydrochloric acid and allowed to stand for 5 minutes. This waiting period is important as the chromate is converted to dichromate during this time. A few crystals of potassium iodide are then added, and the iodine thus liberated is titrated with 0·05 N sodium thiosulphate, using starch indicator. The reactions are represented:

$$2Na_2CrO_4 + 2HCl = \qquad - Na_2Cr_2O_7 + H_2O.$$
$$Na_2Cr_2O_7 + 14HCl + 6KI$$
$$= 2CrCl_3 + 2NaCl \cdot \quad 6KCl \cdot$$

1 ml. of 0·05 N sodium thiosulphate is equivalent to 0·867 mgm. of chromium.

It is necessary to carry the method through quickly or high results are obtained. The present author also found the reduction with alcohol to be somewhat violent.

Direct Method of Jenkins and Hewitt.†

This method is the simplest and most rapid, but is probably also the least accurate. A measured volume of the sample is acidified in the presence of potassium iodide, and the iodine thus liberated is titrated with standard thiosulphate solution. Reduced chromium is not determined by this method.

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* *J. Proc. Inst. Sewage Purif.*, 1939, **1**, 26.   † *J. S. C. I.*, 1940, **59**, 41.

Dickinson's Method for Chromates.

Dickinson * objected to the method of Jenkins and Hewitt on the grounds that it took no account of the iodine liberated by nitrites in acid solutions, and he proposed the following method.

50 ml. of the sample are measured into a stoppered bottle and a few crystals of sodium azide are added. The mixture is acidified with a few ml. of concentrated phosphoric acid, mixed by rotation, and left to stand for several minutes. Excess potassium iodide and 5 ml. of 25 per cent sulphuric acid are then added, and the iodine liberated is titrated with 0·025 N sodium thiosulphate solution, using starch indicator.

Colorimetric Determination of Chromium.

Graham † has shown that the discharge of waste chromium solutions into streams may contaminate wells in the vicinity of the water-course. The concentration of chromium entering potable waters in this way is very small—less than 0·1 p.p.m. —but as our knowledge of the toxicity of chromium is very limited he emphasizes the need for a strict supervision of wells which might be subject to such contamination. The following methods are abstracted from his original paper. Iron and molybdenum in excess of 1 p.p.m. interfere.

Chromates.

The following solutions are required:

(i) Standard potassium chromate solution. Dissolve 0·374 ·gm. of K_2CrO_4 in a litre of water. Dilute 10 ml. of this solution to 1 litre to obtain a solution containing 0·001 mgm. of Cr per ml.

(ii) Diphenyl-carbazide reagent. Dissolve 0·1 gm. in 50 ml. of 95 per cent alcohol and add 200 ml. of 10 per cent (by volume) sulphuric acid. This solution must be stored in a cool dark place.

(iii) Saturated zinc sulphate solution.

(iv) Sodium hydroxide, 10 per cent solution.

(v) Phenolphthalein indicator.

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* *Analyst*, 1940, **65**, 409.   † *J. Amer. Water Works Assoc.*, 1943, **35**, 159.

If the water is of potable quality and free from hydrogen sulphide, the chromate may be determined directly without any preliminary treatment. In this case add 5 ml. of diphenyl-carbazide reagent to 100 ml. of the sample in a Nessler glass. Prepare standards by diluting suitable volumes of the standard dilute chromate solution to 100 ml. in similar Nessler glasses and add 5 ml. of the diphenyl-carbazide to each. After not less than three minutes, but within 60 minutes, compare the unknown with the standards. The result is given by $x \times 10^{-2}$ p.p.m. Cr, where x is the number of ml. of standard chromate solution in the standard which matches the unknown.

If the sample is sewage or contains sulphides, measure 100 ml. into a Nessler glass and add 1 ml. of zinc sulphate solution and two drops of phenolphthalein. Run in the sodium hydroxide from a burette until a faint pink colour is produced and allow the precipitate to settle. Pipette 25 or 50 ml. of the clear supernatant solution and make this up to 100 ml. in a Nessler glass. Add the diphenyl-carbazide reagent and compare with standards as described above. The result is obtained from

$$x/(\text{ml. of supernatant solution pipetted}) \text{ p.p.m. Cr.}$$

Total Chromium.

In order to determine the total chromium present, a preliminary oxidation of the sample is necessary. Add 3 ml. of sulphuric acid and 1 ml. of nitric acid to 100 ml. of the sample and evaporate the solution until white fumes appear. Cool, and add about 50 ml. of water. Make the solution just alkaline by adding 10 per cent sodium hydroxide and then add approximately 5 gm. of sodium peroxide. Boil the solution until the reaction is complete, cool, and filter. Make the filtrate just acid by the addition of dilute (50 per cent by volume) sulphuric acid and make up to 100 ml. with water. Transfer the solution to a Nessler glass, add 5 ml. of the diphenyl-carbazide reagent and proceed as described above.

IRON

Iron is to be found in most waters, in all sewages, and in most trade effluents, but its concentration may vary from less than 1 p.p.m. in a good water supply to several " per cent " in certain trade wastes. It is therefore not possible to give one general method for its determination.

Soft waters corrode iron pipes and boilers more rapidly than hard waters, so that the concentration of iron may rise to an objectionable figure in a soft water. It is an undesirable element in the water supply of a laundry.

Preliminary Test for Iron.

Acidify about 10 ml. of the sample with nitric acid in a test-tube, and boil the mixture for 30 seconds. Cool, and add several drops of a solution of potassium ferrocyanide. A blue colour develops in the presence of iron. If large quantities of iron are present, the blue compound will precipitate.

Colorimetric Method for Iron. (Concentrations less than 40 p.p.m.)

It is preferable where it is possible to use for this determination the ash remaining after the ignition of the total solids. If this ash is available the iron may be determined directly by Walker's method.*

Dissolve the ash by adding 3·0 ml. of concentrated nitric acid and boiling for a few seconds. This boiling is essential as it drives off any nitrous acid which may be present. Then dilute the solution with distilled water and filter through an acid-washed paper into a Nessler glass. Make up the volume to the 50-ml. mark and then add 10 ml. of a 5 per cent solution of potassium ferrocyanide. After standing for not less than 5 minutes the colour is matched with standards containing known amounts of a ferric solution, 3 ml. of boiled concentrated HNO_3, made up to 50 ml. in similar glasses, and 10 ml. of the ferrocyanide solution. The standard which is nearest

* *Analyst*, 1925, **50**, 279.

to the unknown, but less blue, is made to match exactly by running into it from a 10 ml. burette an additional amount of the standard ferric solution.

The standard ferric solution is prepared by dissolving 0·7022 gm. of ferrous ammonium sulphate in 100 ml. of water, adding a little sulphuric acid and warming the solution, and then adding potassium permanganate solution cautiously until a faint permanent pink colour persists. If this is done by titration with a standard permanganate solution, the concentration of the ferric solution can be checked from the volume of permanganate required. This ferric solution is then made up to 1 litre. 1 ml. contains 0·1 mgm. of ferric iron.

TABLE 3

TINTOMETER READINGS FOR THE COLORIMETRIC
DETERMINATION OF IRON BY WALKER'S METHOD

Mgm. of Fe in 60 ml. of solution	Lovibond Tintometer Reading		
	Blue	Yellow	Neutral
0·05	1·2	0·4–0·7	0–0·1
0·10	2·3	0·8–1·2	0·1–0·4
0·15	3·3	1·2–1·7	0·4–0·7
0·20	4·3	1·6–2·2	0·7–1·0
0·25	5·3	2·0–2·7	1·0–1·3

The values apply to a 1-cm. cell only. The blue value is used for the determination of the iron.

The 60 ml. of solution referred to in the heading of column 1 is the 60 ml. of the final coloured solution.

In practice, all the unknowns and the standards should be prepared together up to the addition of the ferrocyanide, 10 ml. of which should then be added to each Nessler glass in turn.

If a Lovibond tintometer is available, the iron may be determined by means of a graph constructed from the colour values given in Table 3. The yellow value varies considerably, and only the blue value should be used for the purpose.

It is essential to guard against accidental contamination of

the ash or materials with rust. Stainless steel crucible tongs are valuable in this connexion.

Colorimetric Determination of Total Iron with Thioglycollic Acid.

Thioglycollic acid reduces ferric iron to the ferrous state, and then reacts with it further to form a red compound which is soluble in ammonia solutions. This is the basis of a deservedly popular method for the determination of the total iron content of water.

Dissolve 7·022 gm. of ferrous ammonium sulphate in a litre of water acidified with a few ml. of concentrated sulphuric acid. This is the stock solution and contains 1·0 mgm. of iron per ml. Dilute 10 ml. of this solution to 100 ml. to give a solution containing 0·1 mgm. of iron per ml., and use this solution for the preparation of colour standards (see below).

TABLE 4

CALIBRATION DATA FOR THE LOVIBOND TINTOMETER FOR THE DETERMINATION OF IRON WITH THIOGLYCOLLIC ACID. 1-CM. CELL

Mgm. Fe per 50-ml. sample	p.p.m. Fe	Red Units
0·1	2·0	0·9
0·2	4·0	1·8
0·3	6·0	2·7

Allow the sample to settle if necessary and decant 100 ml. into a Nessler glass. The sample should not be filtered or some iron may be lost. To a series of similar glasses add 0·2, 0·5, 0·7, 1·0 ml. of the dilute standard iron solution to give a range of standards of concentration up to 1·0 p.p.m. (or a more suitable range) and make the volume up to 100 ml. with distilled water. Add one drop of thioglycollic acid to each Nessler tube and follow this with 1 ml. of approximately 5 N ammonium hydroxide. Mix the contents of each tube by rotation and allow 5 minutes for the colour to develop before comparing the unknown with the standards.

If the sample contains from 1 to 6 p.p.m. of iron, the Lovibond tintometer may be used for the measurement of the colour. This is especially useful if the sample has a natural colour. The figures in Table 4 apply to the determination with a 50-ml. portion of the sample, instead of 100 ml. as described above. The intensity of the red colour plotted against the mgm. of iron present in 50 ml. of the sample is a straight line over the range 0 to 0·3 mgm.

Volumetric Determination of Iron.

Wishart and Lovett described the following method for the determination of iron in trade effluents and sewages.*

Acidify a suitable volume of the sample by the addition of sulphuric acid and add a few small pieces of granulated zinc. The whole of the iron is thus reduced to the ferrous state. From time to time extract a drop of the solution on the end of a glass rod and add it to a drop of ammonium thiocyanate solution on a spot plate. The reduction is complete when no red colour is produced. Filter the solution quickly through glass wool and wash the filter with a stream of water. To the combined filtrate and washings add a further 5 ml. of concentrated sulphuric acid, and titrate the solution with standard potassium permanganate solution until a permanent pink colour is produced. If the sample contains an appreciable amount of chloride the end-point is improved by adding three drops of a solution of diphenylamine (1 gm. diphenylamine in 100 ml. conc. H_2SO_4), which results in the formation of a permanent violet-blue colour when the whole of the iron has been oxidized.

The author prefers to effect a preliminary separation of the iron by acidifying the measured sample with a little hydrochloric acid, filtering, and then precipitating the iron by adding ammonia. The precipitated hydroxide is collected on a paper, and then dissolved in dilute sulphuric acid, followed by reduction and titration with permanganate as described above.

If phosphates are present in any quantity, a measured

* *J. Proc. Inst. Sewage Purif.*, 1935, 1.

volume of the sample should be evaporated to dryness and the residue ignited in a muffle furnace. The iron content of the ash may then be determined by the colorimetric method using potassium ferrocyanide.

ALUMINIUM

The presence of aluminium salts in water or sewage is largely due to the use of alum for coagulation. Aluminium salts may also occur in natural waters and the presence of aluminosilicates renders the separation of the aluminium as hydroxide for its gravimetric determination a tedious and difficult operation. For this reason, the gravimetric method, although a standard method, has been omitted from this work. In its place, a colorimetric method is described. This method, which determines soluble aluminium compounds, is sufficiently accurate for most purposes, and if it is carried out with the aid of a Lovibond colorimeter, its accuracy leaves little to be desired.

Colorimetric Determination of Aluminium.

This method was devised by Hatfield,* and was intended as a control test for water purification plants employing aluminium salts as coagulants. As described, it determines only aluminium in solution; total aluminium could be determined by acidification of the sample prior to filtration.

The solutions required are:

    (i) 0·1 per cent of hæmatoxylin in water;
    (ii) saturated ammonium carbonate solution;
    (iii) acetic acid: 300 ml. glacial acetic acid diluted to 1 litre;
    (iv) standard aluminium solution, containing 0·8366 gm. per litre of pure ammonium alum. 1 ml. of this solution contains 0·05 mgm. Al.

Measure 50 ml. of the filtered sample into a Nessler glass and add 1 ml. of ammonium carbonate solution and 1 ml. of

* *Ind. Eng. Chem.*, 1924, **16**, 233.

hæmatoxylin solution. Prepare standard colour solutions at the same time, containing 0, 0·2, 0·4, 0·6, 0·8, 1·0 ml. of the alum solution, and diluted to 50 ml. with distilled water. After mixing the additions of ammonium carbonate and hæmatoxylin with the solutions, leave to stand for 15 minutes to allow the lavender colour to develop. Then add 1 ml. of the acetic acid, when the colour changes to yellow-brown. After 30 minutes, compare the colour of the unknown with those of the standards. If a tintometer is not available, it may prove an advantage to use a comparator for the purpose.

TABLE 5

TINTOMETER VALUES FOR THE DETERMINATION OF ALUMINIUM BY HATFIELD'S METHOD.   1 CM. CELL

Mgm. Al in 50 ml. of water	Lovibond T Yellow	Red	Ratio: Red/Yellow
0·0	2·8	0·5	0·179
0·2	2·3	0·9	0·391
0·4	1·85	1·35	
0·6	1·5	1·75	1·17
0·8	1·3	2·2	1·65
1·0	1·15	2·6	2·26
1·2	1·05	3·05	2·91
1·4	1·0	3·45	3·45
1·6	0·95	3·9	4·11
1·8	0·92	4·35	4·73

Data for the construction of a tintometer calibration curve are set out in Table 5. The measurements are applicable to colours which have developed for not less than 10 minutes before acidification, and not less than 30 minutes after acidification. It has been found, however, that the ratio of the red units to the yellow units is independent of time after acidification. Therefore, if this ratio is plotted against mgm. Al and used as the calibration curve, it is not necessary to wait for 30 minutes after adding the acetic acid before measuring the colour. The time allowed for the development of the lavender colour before acidification may not be reduced to less than 10 minutes.

MANGANESE

Manganese in excess of 0·1 p.p.m. is undesirable in a water supply. It may find its way into natural waters from minerals in the districts in which they originate or through which they pass. In the light of recent research by Hopkins and McCall,* most of the manganese content of impounded waters may originate in the decomposing organic matter on the bed of the reservoir or in the streams feeding it. In such cases the manganese is present in solution in the form of manganous bicarbonate. An analysis of a manganese-bearing water taken from the bottom of a reservoir is as follows: p_H 7·3, total alkalinity 13·6 p.p.m., CO_2 62·0 p.p.m., dissolved oxygen nil, manganese 15·2 p.p.m., ferrous iron 28·0 p.p.m., appearance, " clear ".†

The methods for manganese determination are all based on the principle of its oxidation to permanganate, followed by determination of the permanganate either colorimetrically or volumetrically. The methods are specific.

Colorimetric Determination of Manganese by the Persulphate Method.

If the water contains less than 2 p.p.m. of manganese, 100 ml. is a suitable portion to take for this determination. If the concentration is expected to be greater than 2 p.p.m., take a proportionately smaller volume of the sample. If necessary, add sufficient distilled water to increase the volume to about 100 ml. and add 2 ml. of concentrated nitric acid, free from oxides of nitrogen, and boil the solution until its volume is reduced to about 30 ml. Add a 2 per cent solution of silver nitrate to precipitate the chloride and 1 to 2 ml. in excess and digest the mixture in a boiling water-bath until the precipitate coagulates and settles readily. Filter the solution and wash the residue with a little distilled water; the total volume of filtrate and washings should not exceed 50 ml.

It is necessary to submit standards to exactly the same

treatment as the sample. A standard manganous solution is prepared by dissolving 0·2873 gm. of potassium permanganate in about 100 ml. of distilled water, acidifying with sulphuric acid, and reducing at a temperature of about 70° C. by adding just sufficient dilute oxalic-acid solution to discharge the colour; the manganous sulphate solution thus produced is cooled and diluted to 1 litre. Then 1 ml. contains 0·1 mgm. of manganese. Portions of 0·2, 0·4, 0·7, 1·0, 1·5, and 2·0 ml. of this solution are each diluted to 50–60 ml. with distilled water, 2 ml. of the nitric acid are added, and the solutions are boiled down to about 30 ml. 1 ml. of the silver nitrate solution is added to each (no precipitate should form, of course), and they are digested in the water-bath along with the unknown solution.

To the unknown and to each standard add 0·5 gm. of pure crystalline ammonium persulphate (which must be free from chloride), and warm on the water-bath until the maximum permanganate colour develops. Then pour each solution into a 50-ml. Nessler glass, make the volume to the 50-ml. mark with distilled water, and compare the unknown with the standards.

Alkaline Earth and Alkali Metals

CALCIUM

The determination of calcium forms part of the usual mineral analysis of water supplies, when it is of particular importance in connexion with the hardness of the supply. The importance of this factor is not restricted to consideration of the suitability of the supply for industrial purposes, but is also involved in the estimation of the nutritional value of the water. The determination of calcium may also be applied as a routine test to waters which are treated with lime, and to sewages and industrial effluents similarly treated. The following two methods are applicable.

Volumetric Determination of Calcium.

Acidify 100 ml. of the sample with hydrochloric acid and boil for a few minutes. Add an excess of ammonia and cool the solution under the tap. Filter off the precipitated iron and aluminium hydroxides and collect the filtrate and washings in the same vessel. Again warm the solution to about 60° C. and add a little ammonia to ensure an adequate excess. Then add 5–10 ml. of a saturated solution of ammonium oxalate and stir the mixture well to assist coagulation of the precipitate. The solution should then be left to cool, stirring once or twice during this period. When cold, the supernatant solution should be clear although some of the precipitated calcium oxalate will almost certainly adhere to the sides of the vessel. Filter the solution through a fine paper and wash the precipitate by decantation until the filtrate is free from oxalate, i.e. when the addition of a drop of lime water to the filtrate fails to give a precipitate. Dissolve the precipitate off the paper

with cold 5 per cent sulphuric acid, collecting this solution in the beaker in which the original precipitation was carried out. Add sufficient of this sulphuric acid to the beaker to dissolve the precipitate, and then add 10–20 ml. of distilled water. Heat the solution to about 60° C. and titrate with a standard solution of potassium permanganate—the N/8 solution used for other determinations is suitable—until a faint pink colour is produced and remains permanent for about 15 seconds. A blank determination is advisable and its value should be subtracted from the titration.

The result, in terms of $CaCO_3$, is given by

$$t \times 6 \cdot 25 \times 1000/(\text{Volume of sample taken}) \text{ p.p.m.,}$$

where t is the net titration in ml. of $N/8$ $KMnO_4$.

Volumetric Determination of Calcium without Separation of Iron.

This method is the one recommended in *Standard Methods for the Examination of Water and Sewage* for analysis of water supplies. It is essentially that of Hale,* and is but little different from that described above. A suitable volume of the water sample, usually 200 ml., is rendered alkaline by the addition of 0·5 ml. of ammonia, and 10 ml. of a saturated solution of ammonium chloride are added. Saturated oxalic acid solution is then added gradually until the solution is just acid to litmus. This is followed by the addition of 5 ml. of saturated ammonium oxalate solution, and the mixture is then boiled for 15 minutes. The precipitate is collected on a filter (a platinum Gooch crucible, previously ignited, is recommended in *Standard Methods*) and washed thoroughly. The precipitate is then returned to the original beaker and dissolved in hot water containing 10 ml. of 50 per cent sulphuric acid, when the oxalic acid liberated is titrated with standard permanganate. A blank determination should be carried through all the stages.

* *J. Amer. Chem. Soc.*, 1907, **29**, 1078.

<center>MAGNESIUM</center>

The determination of magnesium is of special importance for waters intended for boiler-feed purposes, partly on account of the hardness which its salts introduce and partly because magnesium salts, especially the chloride, cause excessive corrosion at high temperatures owing to their dissociation, e.g.

$$MgCl_2 + 2H_2O \rightleftharpoons Mg(OH)_2 + 2HCl.$$
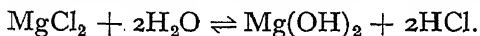
The usual method for determination of the element is often employed, i.e. calcium is first removed, after which the magnesium is precipitated as phosphate, ignited, and weighed.

Gravimetric Determination of Magnesium.

Add about 5 ml. of strong ammonia to 200 ml. of the sample and warm the solution to 70° C. on the water-bath. Add 10 ml. of saturated ammonium oxalate solution in portions of about 2 ml., stirring after each addition, and digest the mixture on the water-bath until the precipitated calcium oxalate settles to leave a clear supernatant solution. Filter off the precipitate, which may be used if desired for the determination of calcium, provided that very little iron is present, and collect the filtrate and washings together. Acidify the solution with hydrochloric acid and concentrate it to about 100 ml. While it is still hot, add 20–25 ml. of a saturated solution of sodium ammonium phosphate, stir, and allow the mixture to cool. Then stir in a few drops of ammonia, sufficient to render the solution distinctly alkaline to litmus, and allow the mixture to stand overnight if possible. Filter through a fluted paper and wash the precipitate with dilute ammonia solution (about 3 per cent NH_3). Redissolve the precipitate in dilute hydrochloric acid, and repeat the precipitation of the magnesium phosphate. Collect the precipitate on an ashless filter paper and wash it with the dilute ammonia solution. Carefully transfer the filter paper and precipitate to a weighed crucible and then place it in a steam-oven to dry the paper. Finally, ignite the crucible and its contents in a muffle furnace, raising the temperature slowly to a red heat. Alternatively, ignite

over a burner, avoiding too rapid heating to redness, as this favours the formation of small pieces of carbon, which are difficult to burn. A burner of the Méker type should be used to complete the ignition. There should be a white residue of magnesium pyrophosphate. 21·84 per cent of the weight of this residue is magnesium. If manganese is present in the sample, manganese phosphate will accompany the magnesium phosphate, and a correction for this must be applied. Having determined the amount of manganese present as described on p. 85, the corresponding weight of phosphate is obtained by multiplying by the factor 2·586.

Volumetric Determination of Magnesium.

First separate the calcium as described under the gravi-metric method, acidify the filtrate and washings with hydro-chloric acid, and concentrate to a volume of about 100 ml. Add 0·25–0·5 gm. of solid ammonium chloride and 4 ml. of a 10 per cent solution of ammonium phosphate ($(NH_4)_2HPO_4$) and 30 ml. of concentrated ammonia solution. Stir the mixture thoroughly and leave to stand overnight. Filter the solution through a No. 40 Whatman filter paper, and wash the residue of magnesium-ammonium-phosphate four or five times with dilute ammonia (1 volume of 0·880 ammonia in 3 volumes of water). Wash the precipitate with 30 per cent aqueous alcohol to remove ammonia. Transfer the paper and precipitate to the beaker in which the original precipitation was carried out and cover it with distilled water. Add a measured excess of 0·1 N hydrochloric acid and a few drops of cochineal indicator. Allow 5–10 minutes for the completion of the reaction, and add more acid if the indicator shows signs of changing from its yellow colour. Finally titrate the solution with 0·1 N sodium hydroxide solution; the end-point is marked by a change in the indicator to a violet colour.

The reactions involved are:

(1) $Mg(NH_4)PO_4 + 3HCl = MgCl_2 + NH_4Cl + H_3PO_4$

(2) $NaOH + H_3PO_4 = NaH_2PO_4 + H_2O.$

(3) $NaOH + HCl = NaCl + H_2O.$
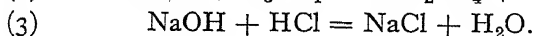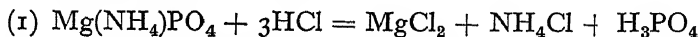
In the final titration the whole of the excess hydrochloric acid is neutralized and the phosphoric acid is neutralized as far as the acid phosphate stage, i.e. " one-third neutralized ". Therefore, if x ml. is the value of the final titration and 10 ml. of acid were added to the phosphate, $10 - x$ is equivalent to two-thirds of the phosphoric acid liberated. . Hence the equivalent in mgm. of Mg is obtained as follows:

1 ml. of 0·1 N NaOH neutralizes completely $\frac{98}{3} \times 10^{-4}$ gm. H_3PO_4. The volume of 0·1 N NaOH required to neutralize completely the H_3PO_4 liberated $= (10 - x) \times \frac{3}{2}$ ml., which is equivalent to $(10 - x) \times \frac{3}{2} \times \frac{98}{3} \times 10^{-4}$ gm. H_3PO_4.

According to equation (1), the liberation of 98 gm. of H_3PO_4 corresponds with a Mg content of 24·3 gm. in the phosphate. Hence the weight of Mg is given by

$$= (10 - x) \times 0 \cdot 001215 \text{ gm.}$$
$$= (10 - x) \times 1 \cdot 215 \text{ mgm. of Mg.}$$

Sodium and Potassium

In order to determine sodium and potassium in a water, all other metals must be removed and the alkali metals finally obtained as their chlorides. Potassium can then be separated from the mixture and the sodium determined by difference. This is naturally a lengthy procedure, and it is usual to shorten it a little by not separating the potassium and calculating the mixed chlorides as sodium chloride.

Gravimetric Determination as Chlorides.

The volume of sample to be taken for the determination may be estimated from the total solids content; sufficient should be taken to give a residue of about 0·5 gm. on evaporation. Evaporate the sample nearly to dryness in a platinum dish, and moisten the residue thoroughly with 1 ml. of hydrochloric acid containing about 20 per cent HCl. Continue the evaporation to complete dryness and char any organic matter

by placing the dish in a muffle furnace at about 500° C. for a few minutes. Cool, moisten the residue with hydrochloric acid and dry on a water-bath. Acidify the residue with a few drops of concentrated hydrochloric acid, add 10 ml. of distilled water and heat on the water-bath to dissolve the soluble part of the residue. Filter the solution and wash the residue several times with hot water. Return the solution to the water-bath and add an excess of hot barium chloride solution. Digest the mixture on the water-bath, stirring at intervals, until the precipitated barium sulphate settles readily to leave a clear supernatant solution. Filter the solution and wash the residue thoroughly. If it is desired, the precipitate may be filtered through a weighed Gooch crucible and used for the gravimetric determination of sulphate. ·

To the filtrate add a slight excess of ·barium hydroxide solution and heat to boiling. Allow to cool and filter, washing the residue with hot water. Add a few drops of concentrated ammonia to the filtrate and a slight excess of ammonium carbonate. Heat the mixture on the water-bath and add a few drops of saturated ammonium oxalate solution. Filter the solution, collecting the filtrate in a platinum dish, and evaporate to dryness on the water-bath and then heat the residue over a burner to expel ammonium salts. The temperature should not be allowed to rise above a very dull red heat during this operation. If the residue contains carbon, oxidize this by evaporation with a few drops of concentrated nitric acid. Moisten the residue with a little concentrated hydrochloric acid, evaporate to dryness, and finally heat to a very dull red heat over a burner. Cool in a desiccator and weigh. Dissolve the mixed chlorides in 5 ml. of warm water, filter through a 5-cm. ashless filter paper and wash with the minimum of water. Return the paper and residue to the platinum dish, dry, ignite, and weigh. The difference between the two weighings gives the weight of mixed sodium and potassium chlorides.

Determination of Potassium as Chloroplatinate.

Acidify the solution of mixed chlorides obtained from the above determination with a few drops of hydrochloric acid,

and then add a volume x ml. of 10 per cent platinic chloride solution, where $x = $ (gm. of NaCl + KCl in solution)$/$0·03 ml. Evaporate the mixture to a syrupy consistency on the water-bath, when potassium chloroplatinate will be precipitated. Allow the mixture to cool and then add 80 per cent aqueous alcohol and filter through a dry paper. Wash the precipitate with alcohol until the filtrate is colourless. Dry the paper in the oven, and then dissolve the precipitate in a little hot water, collecting the solution in a weighed platinum dish. Evaporate the solution and dry the residue and finally weigh.

Potassium chloroplatinate is K_2PtCl_6, and contains 16·09 per cent of its weight of potassium.

Results are often calculated as parts per 100,000 Na_2O and K_2O. They may also be returned as p.p.m. of the oxides, the metals, or the chlorides.

Residual Chlorine, Salts, Fluorine, Silica

RESIDUAL CHLORINE

The " chlorine residual " is the concentration of hypochlorite or of chloramines (calculated as chlorine) which remains in a water which has been chlorinated. The rate at which chlorine reacts with the impurities present in the water varies considerably with the composition of the water, particularly with its ammonia content and its p_H. Consequently a value for residual chlorine has little meaning unless it is referred to the contact time, i.e. the time which has elapsed between the addition of the chlorine to the water and the determination of the residual, or to some definite stage in the water purification process. Generally speaking, the residual chlorine present in a sample drawn from a consumer's tap should be very small, but it is not likely to be zero unless the tap is situated towards the end of the service main. o-Tolidine is the most popular reagent for the determination of chlorine residuals, but it is not specific under the acid conditions required for the test, and it reacts in the same way with any oxidizing agent. Ferric iron, manganic salts, and nitrites are the most likely substances to interfere. There are many modifications of the o-tolidine test which have been proposed to overcome the interference of one or more of these substances and the modification described below appears to be that most widely applicable.

The neutral starch-iodide method is not subject to such interference, but it is probably less accurate for the determination of small residuals. Ozone, of course, would interfere

with this test, but until the ozonation of water supplies becomes more widely adopted, this factor need hardly be considered.

When the water has been treated by the combined use of ammonia and chlorine, the residual chlorine, which may be partly or wholly in the form of chloramines or nitrogen trichloride, takes longer to react with *o*-tolidine. There is at present no known method of distinguishing between chlorine residuals due to hypochlorites and those due to chloramines, with the possible exception of the electrochemical titration with sodium arsenite recently described by Marks and Glass.* This method eliminates interference from the common oxidizing agents. The original paper must be consulted for details.

Determination of Residual Chlorine by the *o*-Tolidine Method.†

Solutions required:

  (i) *o*-Tolidine solution. Prepare 500 ml. of dilute hydrochloric acid, 1 vol. concentrated HCl to 3 vols. distilled water. Grind 1·0 gm. of *o*-tolidine with a little of this acid in a mortar until solution is complete, then wash the solution into a litre graduated flask with the dilute acid, and add what remains of the acid to the flask. Make up the volume to 1 litre with distilled water.

     This solution should be stored in a brown glass bottle in the dark.

  (ii) Dilute hydrochloric acid containing 300 ml. of concentrated acid per litre.

  (iii) Special dilution water. Prepare a 1 in 10 dilution of laboratory reagent sodium hypochlorite (containing about 12 per cent available Cl). Add 0·1 ml. of this diluted solution to 1½ litres of distilled water and leave the mixture to react for 30 minutes. Then boil the water for 30 minutes and cool. This water should be prepared fresh daily as required.

* *J. Amer. Water Works Assoc.*, 1942, **34**, 1227.
† Scott, *J. Amer. Water Works Assoc.*, 1934, **26**, 9.

(iv) Standard chlorine water. The chlorine water used for the determination of chlorine demand may be used as stock solution (cf. p. 50). From this solution, freshly standardized, prepare a dilute standard solution containing 10 mgm. per litre, using the special dilution water for the purpose. Then, 1 ml. of this dilute solution diluted to 100 ml. will correspond with a water containing 0·10 p.p.m. residual chlorine.

A standard solution of sodium hypochlorite of equivalent concentration may be substituted for the above.

Prepare a series of standards by adding to 100-ml. Nessler tubes 0, 2, 4, 6, 8, and 10 ml. of the dilute standard chlorine water, and make up the volume to 100 ml. in each case with the special dilution water. Each of these solutions and the sample to be tested should be warmed carefully to 20° C. Then pour 100 ml. of the sample into a similar Nessler tube. To each tube add 1 ml. of the o-tolidine solution and 1 ml. of the dilute hydrochloric acid and mix thoroughly. Then place all the tubes in a dark cupboard and allow the colour to develop. After at least 5· minutes, observe the colour of the unknown solution at frequent intervals, and as soon as it appears to have reached its maximum intensity, compare it with the standards. This determination must be completed within 15 minutes of adding the o-tolidine. At no time may the sample, the standard chlorine water, or the standards be exposed to direct sunlight.

Permanent colour standards may be prepared, but their use is restricted to rigorously standardized conditions, for which see *Standard Methods* (cf. footnote, p. 13).

If manganese is present in a concentration greater than 0·01 p.p.m., the starch-iodide method should be employed.

Determination of Residual Chlorine with Starch-Iodide.

A solution of potassium iodide containing 75 gm. KI and 100 ml. of ethyl alcohol per litre is required. Freshly boiled

and cooled distilled water should be used to prepare this solution. Standard sodium thiosulphate is also required, $N/50$ or $N/100$ (i.e. 4·966 or 2·483 gm. per litre respectively) and should be standardized against potassium permanganate or iodine each time it is used. (If $N/40$ solution is used in connexion with the oxygen consumed determination, it may conveniently be used as a stock solution.)

It may not be out of place to describe the preparation of the starch solution required. Mix thoroughly in a mortar approximately 1 gm. of potato starch and about 10 ml. of distilled water. Pour the resultant paste into 200 ml. of boiling water, stir in, and leave to cool. If any precipitate should settle, decant the clear solution only into the stock bottle. The addition of preservatives, such as salicylic acid, is often recommended; it is better to make fresh solutions weekly.

To determine the residual chlorine in a sample, measure 1 litre into a porcelain dish and add 10 ml. of the potassium iodide solution from a pipette, holding the orifice beneath the surface of the water. Mix gently with the pipette and allow 5 minutes for the reaction to take place. Then add 5 ml. of starch solution and titrate with the standard solution of sodium thiosulphate. A 5- or 10-ml. burette should be used, and the mixture should be well stirred after each addition of thiosulphate.

CHLORIDES

The chloride content of waters and effluents varies over a wide range. Natural unpolluted waters do not normally contain more than 1 or 2 parts per 100,000 unless there is some special circumstance in the geology of the district through which they pass, while sewages and sewage effluents contain 7 to 14 parts per 100,000 or more, according to the industries of the town. Trade effluents may contain very high proportions of chlorides. In general, however, the same analytical methods are applicable to all classes of waters, the reaction with silver nitrate solution being universally adopted.

For waters containing up to 5 parts per 100,000 of chloride

(expressed as Cl), 100 ml. are pipetted into a beaker and a few drops of phenolphthalein solution are added. If a pink colour is produced, dilute nitric acid is added drop by drop until the colour is discharged. If the water is acid, a slight excess of caustic soda solution should be added first so as to produce a definite pink colour, followed by the nitric acid as described above. The solution is then titrated with silver nitrate solution containing 2·395 gm. per litre $AgNO_3$,* using 2 ml. of a 5 per cent solution of potassium chromate as indicator. The end-point is marked by the appearance of a red-brown precipitate of silver chromate. 1 ml. of the standard silver solution is equivalent to 0·5 mgm. of Cl.

Turbid solutions should be filtered before the titration is attempted; it is convenient to use the filtrate from the suspended solids determination for this purpose. For sewages and effluents, 25 or 50 ml. of the sample should be sufficient. It is not possible to indicate the most convenient volume for the titration of trade wastes, since the chloride concentration varies so widely. The volume of indicator added should be $\frac{1}{50}$ of the volume taken. It is also quite impossible to forecast a method applicable to all trade effluents owing to the possibility of the presence of interfering substances. If the interference is due to intense colour or even opacity, the electrometric method described in the following section may be used. It is, in fact, recommended for general use in preference to the method described above.

Electrometric Titration of Chlorides.

The electrometric method described below was devised by Callan and Horrobin for the determination of chlorides in solutions of dyestuffs.† It depends on the cell

$$Ag \mid AgCl \parallel XCl \mid Ag.$$
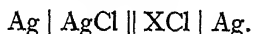
Two lengths of pure silver wire, about 3 in. long and 18 S.W.G., are required as electrodes. One of these is coated with a thin

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* Standardize against sodium chloride solution, 1·648 gm. per litre. 1 ml. contains 1·0 mgm. Cl.

† *J. S. C. I.*, 1928, **47**, 329.

film of silver chloride by using it as anode for the electrolysis of a chloride solution, for which purpose potassium chloride, approximately o·1 N, will serve. An ordinary 2-volt dry cell is suitable as a source of E.M.F., and the current should be allowed to flow for about $\frac{1}{2}$ hour. The Ag/AgCl electrode thus obtained should be removed from the chloride solution and washed thoroughly with a jet of distilled water from a wash-bottle, when it is ready for use in the preparation of the standard half-cell. A 4-oz. wide-mouthed bottle is a convenient container, and it is preferable that it be made of brown glass. It should be fitted with a rubber stopper through which a small hole is bored to allow the Ag/AgCl electrode to pass through. This is pushed through from below, taking care not to disturb the chloride film on that part of the wire which will be inside the bottle. A second hole is bored in the stopper to admit a salt bridge containing saturated sodium sulphate solution (see p. 24 for a description of the bridge). The bottle is then filled about half-way with 10 per cent nitric acid and one drop of the standard silver nitrate solution to be used for the titration is added. When the Ag/AgCl electrode is suspended in this solution the same electrical conditions exist as mark the end-point of the titration.

A 250-ml. squat beaker is desirable for the titration vessel. About 75 ml. of 10 per cent nitric acid are added to this and 25 or 50 ml. of the sample are run in from a pipette. The second silver wire is suspended in this solution. The two vessels are connected by means of the salt bridge. The silver electrode is connected with wire to a morse-key which is in turn connected to one terminal of a sensitive galvanometer. The other terminal of the galvanometer is connected directly to the Ag/AgCl electrode. (See diagram, fig. 2, p. 23.) On pressing the key, a marked deflection of the galvanometer needle should occur. Standard silver nitrate solution is then run from a burette into the beaker, stirring vigorously after each addition, until there is no deflection of the galvanometer needle on pressing the key. When this stage is reached, the silver electrode in the beaker has the same potential as the Ag/AgCl electrode in the standard half-cell. The same con-

ditions prevail in the beaker as in the bottle, i.e. metallic silver is in contact with solid silver chloride, which is in equilibrium with its saturated solution in dilute nitric acid (sufficient dissolves from the film on the Ag/AgCl electrode to ensure this) and a slight excess of silver nitrate. The addition of a further drop of silver nitrate should produce a deflection of the galvanometer needle in the direction opposite to that which has prevailed hitherto.

The electrical connexions will doubtless be effected with copper wire. In order to avoid unwanted potentials, the joints of silver and copper should be protected from moisture by coating with wax or, preferably, by embedding them in sealing-wax. The silver electrode is supported by passing it through a cork which can be held in a clamp. The standard half-cell requires occasional renewal, and the silver chloride film should be removed from the Ag/AgCl electrode by means of old emery cloth before attempting to deposit a new film.

SULPHATE

The gravimetric determination of sulphate as barium sulphate is the most accurate method for the analysis of natural waters, and it is best carried out in conjunction with the determination of sodium. For boiler-waters and other waters containing a fairly high proportion of sulphate, the following volumetric method is sufficiently accurate and is much quicker.

Determination of Sulphate by the Benzidine Method.*

Solutions required:
- (i) Benzidine hydrochloride, 11 gm. dissolved in 500 ml. of 1 per cent hydrochloric acid.
- (ii) Standard sodium hydroxide solution (N/10).
- (iii) Phenolphthalein indicator. ·

* Schroeder, *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 403.

Pipette 10 ml. of the benzidine solution into a 250-ml. conical flask, and add 50 ml. of the filtered sample. Mix the solutions and allow 10 minutes for completion of the reaction. Filter the solution until the filtrate is clear and test for complete precipitation of the sulphate by adding a few drops of the benzidine solution to the filtrate. If any further precipitate is formed, repeat the precipitation with the filtrate and collect all the precipitate on the same filter. Wash the precipitate on to the filter with the minimum volume of distilled water, and continue washing until the filtrate is free from chloride, using small portions of distilled water each time. The total volume of water used for these washings must not be much greater than 25 ml.

Fold the filter paper carefully and return it to the conical flask in which the precipitation was carried out, and add 20–30 ml. of distilled water and a few drops of phenolphthalein. Stopper the flask and shake vigorously until the filter paper is reduced to a pulp. Add standard sodium hydroxide solution from a burette a few drops at a time and shake the mixture thoroughly after each addition. The titration is complete when the pink colour produced by the sodium hydroxide remains permanent when the flask is shaken vigorously for at least half a minute.

The result may be recorded in terms of either sodium sulphate, Na_2SO_4, or sulphate, SO_4''. 1 ml. of N/10 sodium hydroxide is equivalent to 7·1 mgm. Na_2SO_4 or 4·8 mgm. SO_4''. If the result is required in grains per gallon, a 70-ml. portion of the sample should be taken. If the final titration requires less than 1·5 ml., the determination should be repeated using 100 ml. of the sample; also, if the final titration requires more than 12 ml., 25 ml. of the sample should be taken for a repeat determination.

PHOSPHATE

The colorimetric determination of phosphate is sufficiently accurate for most purposes, and it is far simpler and quicker than the lengthy gravimetric method, which often involves a

preliminary concentration of a large volume of the sample. Griggs' method * may be employed; hydroquinone (quinol), ammonium molybdate, and the phosphate react to produce a blue colour (molybdenum blue), the intensity of which is directly proportional to the concentration of phosphate present. The solutions required are:

  (i) 5 per cent ammonium molybdate solution in approximately 5 N sulphuric acid;

 (ii) a 20 per cent aqueous solution of sodium sulphite;

(iii) a 0·5 per cent solution of hydroquinone in water to which has been added 1 ml. of N sulphuric acid per 100 ml.;

(iv) a standard phosphate solution. A suitable concentration is obtained by dissolving 0·2865 gm. of pure dry potassium dihydrogen phosphate (KH_2PO_4) in a litre of distilled water. 1 ml. of this solution contains 0·20 mgm. of PO_4'''.

Filter the sample and measure 50 ml. into a 100-ml. Nessler glass. Into a similar glass measure 3 ml. of the standard phosphate solution and make up to 50 ml. with distilled water. Add to each solution 2 ml. of ammonium molybdate, 2 ml. of sodium sulphite, and 2 ml. of hydroquinone solution, and mix. After standing for 30 minutes, transfer the unknown solution to a 50-ml. burette and run it slowly into an empty Nessler glass, identical with that containing the standard colour, until the colour, viewed through the depth of the liquid, matches that of the standard held alongside. Then add distilled water to the Nessler glass now containing sufficient of the unknown solution to match the colour of the standard, to make up the volume to 50 ml., and again compare its colour with that of the standard. The effect of this addition of distilled water is usually to make the colour contained in this volume of the unknown solution appear rather less intense, and it becomes necessary to add a further volume from the burette. When the final adjustment of colour has

been made, the volume of the unknown solution required contains exactly the same amount of phosphate as the standard, i.e. 6×10^{-4} gm. of PO_4'''. Hence the result is given by

$$\frac{6 \times 10^{-4}}{V} \times 10^6 = \frac{600}{V} \text{ p.p.m. } PO_4''',$$

in which V is the volume of the unknown solution (in ml.) required to match the standard.

It is often an advantage to use a standard colour solution containing half the concentration of phosphate of the standard quoted above, i.e. 1·5 ml. of the standard potassium phosphate solution in 50 ml. of distilled water.

TABLE 6

COLORIMETRIC DETERMINATION OF PHOSPHATE: LOVIBOND TINTOMETER READINGS FOR A 1-CM. CELL. TEMP. 18° C.

Mgm. PO_4''' in 50-ml. sample	Tintometer Readings Blue	Yellow	Red
0·2	0·9	0·2	0·1
0·4	1·8	0·4	0·2
0·6	2·7	0·6	0·3
0·8	3·6	0·8	0·4
1·0	4·5	1·0	0·55
1·2	5·4	1·2	0·7

The blue reading only is used for the determination.

It is important that the 30-minute reaction time be adhered to. If a Lovibond tintometer is available, the colour of the unknown solution may be measured accurately. A graph constructed from the data given in Table 6 may then be used to convert the colour measurements into mgm. PO_4'''. The data given in the table were obtained by following exactly the method outlined above *except* that the hydroquinone solution used contained 1·0 gm. per 100 ml. of acidulated water. Under these conditions the method is accurate to within 0·3 p.p.m. PO_4''' over the range 0–40 p.p.m. If the concentration of phosphate is greater than 40 p.p.m., 25 ml. of the sample should be taken instead of 50 ml.

This method is especially suitable for the determination of phosphates in boiler water, but if pyro- or meta-phosphates are present, as is the case in phosphate-conditioned waters, a preliminary treatment with acid is necessary. Neutralize 50 ml. of the filtered sample—the volume of acid required will be known from the total alkalinity determination—and then add 5 ml. of N acid. Boil the solution for several minutes and then cool. Add 5 ml. of N sodium hydroxide and make up to 100 ml. in a graduated flask. Take 50 ml. of this solution for the determination. The method is subject to some interference from silicate, but this will not normally be serious.

SULPHIDES

The concentration of soluble sulphides in natural waters and purified sewages is normally very small, and it is generally sufficient to apply a qualitative test for their presence. This is done by boiling a portion of the sample with solid ammonium carbonate and testing the vapours evolved with lead acetate paper on which ammonium sulphide produces a black stain. When, however, the concentration of sulphide is sufficiently high, as in sulphur dye wastes, for example, it may be determined as follows.

A 500-ml. round-bottomed flask is fitted with a still-head and a condenser. A filter funnel is connected by its stem to the end of the condenser, and its wide end is just submerged in dilute (0·1 N) caustic soda contained in a beaker. About 250 ml. of distilled water are introduced into the flask and 15 to 20 gm. of solid ammonium carbonate are added. A measured volume of the sample is run into the flask. The solution is then boiled to distil over the sulphide as ammonium sulphide. When it is considered that the whole of the sulphide has distilled—about one hour should be sufficient—the bunsen burner is taken away, the still-head disconnected, and a strip of lead acetate paper is held in the steam within the neck of the flask. If no stain appears on the paper the distillation is complete.

The sulphide content of the distillate is then determined.

The distillate and washings from the funnel and condenser are made up to 500 ml. in a standard flask, and a suitable aliquot of this solution is taken for titration with potassium ferricyanide solution containing 3·29 gm. per litre.

If the distillate is yellow, the potassium ferricyanide is added from a burette until the mixture is almost white, when a few drops of a fresh solution of sodium nitro-prusside are added as indicator. If the solution is almost colourless at the start, the indicator is added before the ferricyanide. The addition of the indicator causes the formation of an intense blue to violet colour, and the titration is continued until this colour is discharged. The reaction is

$$2K_3Fe(CN)_6 + K_2S = 2K_4Fe(CN)_6 + S.$$
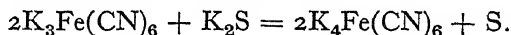
The finely divided precipitate of sulphur appears almost white. 1 ml. of the $K_3Fe(CN)_6$ solution is equivalent to 0·16 mgm. of S.

An alternative method which is applicable to clear and almost colourless solutions without distillation is an adaptation of the original titration of Volhard.* The solution is rendered ammoniacal and titrated with standard silver nitrate solution, when silver sulphide is precipitated. It is necessary to employ an external indicator to determine the end-point, and a solution of p-dimethyl-amino-benzal-rhodanine in acetone is suitable for this purpose. The indicator solution is spotted on to a filter paper and a drop of the sulphide solution being titrated is placed over it. When the solution contains a trace of silver, a deep red colour develops on the paper. The end-point is very sharp and the method can be recommended.

THIOCYANATES

The presence of the thiocyanate ion in sewage is due to a discharge of gas liquor or chemical waste. Its presence is easily detected by acidification of a portion of the sample, followed by the addition of a drop of iron alum solution.

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* *Ber.*, 1874, 7, 100.

The blood-red colour of ferric thiocyanate appears immediately. In dilute solution, the colour disappears on boiling and reappears on cooling. This simple test may be applied in a semi-quantitative estimation of the proportion of gas liquor present in a sewage. It is necessary to have also a sample of the gas liquor, dilutions of which are prepared in Nessler glasses, acidified, and iron alum solution added. The proportion of gas liquor present in the sewage is then obtained by comparison of the colour of the sewage sample after addition of acid and iron alum with the range of " standards ". The only other compounds which give this colour with iron are the thio- and perthio-carbonates which are met with only rarely in discharges from certain chemical processes.

The following method for the determination of thiocyanates is that usually adopted for spent gas liquors * (at least in so far as the separation is concerned). It is equally applicable to more dilute solutions, such as sewages, but a larger volume of sample must be taken.

25 ml. of the liquor are acidified with sulphuric acid and warmed to about 40° C. Several drops of a saturated iron alum solution are added, when any ferrocyanide present is precipitated as Prussian blue. The precipitate, which tends to be colloidal, is removed by filtration through paper pulp in a Gooch crucible. A suction pump is necessary for this. After washing the pulp with an equal volume of distilled water, the filtrate is treated with a moderate excess of sodium sulphite—or meta-bisulphite—and the mixture heated to 60° C. There should be a distinct smell of sulphur dioxide. A 10 per cent solution of copper sulphate is then added until the blue colour of the copper persists, when the mixture is heated to incipient boiling. White cuprous thiocyanate is precipitated, and after cooling it is separated by filtration and washed with hot water. The filtrate from this may be used for the determination of chlorides by titration with silver nitrate (see p. 98). The paper and precipitate are then transferred back to the beaker in which the precipitation was carried out, 50 ml. of 4 per cent caustic soda solution are added,

* Key, " Gas Works Effluents and Ammonia ", *Inst. Gas Eng.*

and the mixture is boiled. The thiocyanate is thus taken up up by the sodium and the copper is converted to hydrated copper oxide. The solution is filtered through alkali-resistant paper (Whatman No. 54), the residue washed thoroughly, and the total filtrate acidified with dilute nitric acid and made up to 250 ml. with distilled water. 50 ml. of the solution are then titrated with 0·1 N mercuric nitrate solution, using iron alum as indicator. The end-point is marked by the disappearance of the red colour.

1 ml. of 0·1 N mercuric nitrate is equivalent to 0·0076 gm. NH$_4$CNS.

It is more usual to titrate the final acid solution of thiocyanic acid with silver nitrate. The advantage of mercuric nitrate is that no bulky precipitate is produced and occlusion of thiocyanate in the precipitate is thus avoided.*

CYANIDES

Cyanides occur in wastes from photographic printing works and from chemical works, and thus find their way into sewage. The dangers arising from such discharges are liable to be over-estimated and the tendency to prohibit altogether the discharge of cyanide wastes into sewers is to be condemned. The very small concentration of cyanide in a photographic wash-water is quite harmless, and there is no reason why it should not enter the public sewer. It is questionable whether the concentration is usually sufficiently high to allow its determination by ordinary chemical means. This section is really included to cover the somewhat rare cases of the discharge of cyanides in waste waters from chemical works and from electroplating processes. There is also the possibility of cyanides appearing in streams and drainage waters owing to the practice of tipping or burying the solid waste cyanide used for the case-hardening of steel.

* Williams, *J. S. C. I.*, 1939, **58**, 77.

Liebig's titration of cyanide by silver nitrate is based on the reaction

$$2KCN + AgNO_3 = KAg(CN)_2 + KNO_3.$$
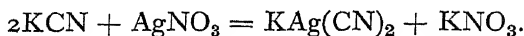
A minute excess of silver nitrate causes an opalescence by the precipitation of silver cyanide. If the titration is carried out in feebly ammoniacal solution in the presence of diphenylcarbazide, the end-point is more clearly seen.[*] The diphenylcarbazide acts as an adsorption indicator, and its natural pink colour changes to a very pale violet on the colloidal precipitate of silver cyanide produced at the end-point. The method is recommended for very dilute solutions of cyanides. Chlorides do not interfere in ammoniacal solution provided their concentration is low.

FLUORINE

The presence of fluorine in water supplies has received considerable attention since 1931, when it was shown by Miss M. C. Smith and her colleagues [†] to be responsible for the condition known as dental fluorosis, or mottled enamel. Very small amounts of fluorine are involved, usually less than 5 p.p.m. Many methods of determination have been proposed, and some of these have recently been examined by a Committee of the American Water Works Association.[‡] It was found that there was very little to choose between the methods as regards accuracy, but for simplicity Scott's modification [§] of Sanchis's original method[||] is unsurpassed. This method is as follows.

Scott's Modified Sanchis Method for Fluorine.

0·43 gm. of zirconium oxychloride is dissolved in 50 ml. of water, and a solution of 0·1 gm. of sodium-alizarin-monosulphonate (alizarin-S) in 50 ml. of water is added to it. 70

[*] Wellings, *Analyst*, 1933, **58**, 331.
[†] *Arizona Agr. Exper. Sta. Tech. Bull.*, No. 32 (1931), No. 43 (1932), No. 45 (1933).
[‡] *J. Amer. Water Works Assoc.*, 1941, **33**, 1965–2017.
[§] Ibid., 2018.   [||] *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 134.

ml. of the mixed solution are diluted to 1 litre with a mixed solution of hydrochloric and sulphuric acids, each approximately 1·35 N.* If a maximum sensitivity over the range 0 to 0·5 p.p.m. is required, the acids should each be 1·5 N.

5 ml. of the reagent are added to 100 ml. of the water under test in a Nessler glass, a series of standards of known fluoride content being prepared at the same time. In the absence of fluorine the colour is pink; increasing quantities of fluorine cause a transition to yellow. The standard fluoride solution recommended by Sanchis is prepared by dissolving 2·21 gm. of dry sodium fluoride in 1 litre of water, subsequently diluting 10 ml. of this stock solution to 1 litre, when a solution containing 0·01 mgm. of F per ml. is obtained. A suitable range of standards may then be made by diluting 0, 2·5, 5·0, 7·5, 10, 15, 20, 25, and 30 ml. of this solution to 100 ml., covering the range 0 to 3·0 p.p.m.

There is still some doubt about the interference of chlorides and sulphates in this determination. Scott quotes 250 p.p.m. of SO_4'' and 500 p.p.m. of Cl' as the permissible limits, but there are other views on the subject.† Goodwin and Litton ‡ have removed sulphates by precipitation with barium chloride, settlement of the precipitate, and decantation. Iron and aluminium, which also interfere, may be removed by aeration of the sample, followed by filtration through fine paper.

The investigations of Dean and Elvove § on the fluorine contents of the water supplies of a number of American cities showed a range of concentration of 0·6 to 4·4 p.p.m. They concluded that waters containing less than 1 p.p.m. could be regarded as safe, but it appears that concentrations greater than 1 p.p.m. will produce mottled enamel in at least 40 per cent of the population served, while 6 p.p.m. produces more serious symptoms in a high proportion of the population and affects the whole of the population with dental fluorosis.

* Scott, *J. Amer. Water Works Assoc.*, 1942, **34**, 522.
† Cf. Goudey, *J. Amer. Water Works Assoc.*, 1941, **33**, 2213.
‡ *Ind. Eng. Chem.*, 1941, **33**, 1046.
§ *U.S. Publ. Health Rep.*, 1937, **52**, 1249.

Silica

The determination of silica is of special importance in connexion with boiler-feed waters and boiler-waters. Provided that a sufficiently large sample of the water is available, silica may be determined gravimetrically by the method described in any of the larger textbooks on analytical chemistry; such a method necessarily involves evaporation of the sample to dryness. The colorimetric determination as silicomolybdate is to be preferred when speed and reasonable accuracy are desired.

Colorimetric Determination of Silica.

The following solutions are required:

(i) Borax buffer solution, p_H 10, prepared from (a) a solution of 12·4 gm. of boric acid in 100 ml. of N/10 caustic soda and 900 ml. of water; (b) N/10 caustic soda. These solutions are mixed in the proportions 6 volumes of (a) to 4 volumes of (b).

(ii) 111 gm. of anhydrous calcium chloride in a litre of water.

(iii) A 10 per cent solution of ammonium molybdate.

(iv) Dilute hydrochloric acid, prepared by diluting 3 volumes of concentrated acid to 5 volumes with distilled water.

(v) Potassium chromate solution, 0·63 gm. K_2CrO_4 per litre.

(vi) A 1 per cent solution of borax.

All the solutions, except the potassium chromate and borax, must be stored in containers from which they will dissolve the minimum of silica. Pyrex glass bottles are suitable for all except the alkaline buffer solution, which must be stored in a rubber- or resin-lined container.

Measure 100 ml. of the sample and precipitate any phosphates by adding 50 ml. of the alkaline buffer solution and 2 ml. of the calcium chloride solution. Stir the mixture and

set aside for 2 hours to allow the calcium phosphate to coagulate and settle. Coagulation may be assisted by occasional stirring during this time. Filter the solution, and collect 50 ml. in a 100-ml. Nessler glass. Acidify with 1 ml. of dilute hydrochloric acid, and add 2 ml. of ammonium molybdate solution and then allow 15 minutes for the colour to develop. During this time, prepare standard colour solutions from the potassium chromate solution, taking appropriate volumes as indicated by Table 7 in a series of Nessler glasses. To each

TABLE 7

COLOUR STANDARDS FOR SILICA

Ml. Potassium Chromate Solution.	SiO_2 mgm.	Ml. Potassium Chromate Solution	SiO_2 mgm
0·0	0·0	8·0	0·8
1·0	0·1	9·0	0·9
2·0	0·2	10·0	1·0
3·0	0·3	11·0	1·1
4·0	0·4	12·0	1·2
5·0	0·5	13·0	1·3
6·0	0·6	14·0	1·4
7·0	0·7	15·0	1·5

After Swank and Mellon (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 348; cf. *Analyst*, 1934, **59**, 773).

standard then add 25 ml. of 1 per cent borax solution and make up the volume to a total of 55 ml. with distilled water. These standards are permanent. Compare the colour of the unknown with the standards, looking down the tubes held over a white plate and facing a north window. The result is given by (mgm. SiO_2 corresponding to standard matching the unknown) × 30·4 p.p.m.

A blank determination on silica-free water should be carried out as a check on the reagents. As these must inevitably dissolve some silica during storage, this should be done each time they are used unless it is found by experience to be unnecessary. The amount of silica thus found to be apparently in the silica-free water must then be deducted from the result.

CHAPTER XII

Sewage Effluents, Grease, Fats

RELATIVE STABILITY TEST FOR SEWAGE EFFLUENTS

Methylene-blue is used as an indicator to mark the exhaustion of available oxygen in an effluent during incubation. The test is valuable for works control as, in the case of doubtful effluents, the result is obtained in less time than is taken by the permanganate incubation test (cf. p. 46) or by the B.O.D. determination (cf. p. 54).

A 6-oz. bottle fitted with a ground-in glass stopper is filled completely with the effluent, the liquid being poured in quietly, taking care to avoid splashing. Any bubbles of air which may adhere to the sides of the bottle are removed by gently tapping the bottle with a glass stopper. o·4 ml. of a solution of pure methylene-blue (o·5 gm. per litre) is added, being run into the bottle from a graduated pipette whose tip is held well down below the surface of the liquid. The stopper is then replaced and the contents mixed by vigorous rotation of the bottle, which is then placed in an incubator at 65° F. The mixture is observed at intervals during the first day and thereafter at daily intervals. The time taken for the blue colour of the indicator to disappear is noted.

For a sample to be judged satisfactory, the methylene-blue must not be reduced during five days' incubation.

Relative stability is defined in *Standard Methods* as " the per cent ratio of oxygen available as dissolved, nitrite, and nitrate oxygen to the total oxygen required to satisfy the biochemical oxygen demand ". The exact relationship between the time taken to reduce the methylene-blue, in days (t),

and the relative stability (s), is given by the equation

$$s = 100 \times (1 - 0.794^t) \text{ per cent.}$$

The conditions for the American test are slightly different, 150 ml. of the sample being used and incubation carried out at 20° C.

GREASE

This determination is usually of interest only for the examination of sewages and certain industrial effluents. There is no standard method and there has been much controversy. The methods used depend on the selective solution of the grease in an organic solvent and the result obtained depends on the solvent used. Fales and Greeley * have recently agitated for a definition of " grease " in sewage and for a standardized procedure for its determination. All or only some of the substances belonging to the groups fatty acids, soaps, oils of all kinds, and waxes may be regarded as " grease " by different chemists. It is certain that all are likely to occur in an industrial sewage. It should be pointed out, however, that a standard procedure would be of less value to the chemist than a more complete knowledge of the components of the greases extracted by those solvents in most common use—ethyl ether, petroleum ether, and chloroform. At present it is known that with any one sewage the use of chloroform will result in the highest, while the use of petroleum ether will result in the lowest value for the grease content. There is also a tendency for the ratio (grease extracted by chloroform)/(grease extracted by petroleum ether) to be constant for any one sewage. There is room for improvement in this position.†

Determination of Grease.

The well-known Roese-Gottlieb method for fat in milk is useful for trade effluents. An extraction apparatus of a design

* *Proc. Amer. Soc. Civil Eng.*, 1942, **68**, 193.

† Since the above was written, Holroyd (*J. Proc. Inst. Sewage Purif.*, 1941, 157) and Jepson and Klein (ibid., 158) have reported that the differences between the results obtained with different solvents are due to the varying solubilities of iron and calcium soaps in the solvents.

similar to that shown in the figure (fig. 5) is required.   If ethyl or petrol ether is to be used for the extraction, the upper layer will have to be syphoned off and the end of the syphon tube will need to turn upwards as illustrated, but if chloroform is to be used, the end of the syphon tube must reach the bottom of the container and open downwards.   10 ml. of the sample are pipetted into the apparatus and 0·5 ml. of ammonia is added.   This is followed by 10 ml. of 95 per cent alcohol and the liquids are mixed well.   25 ml. of the solvent are then added, the container is stoppered, and the mixture is shaken vigorously for 30 seconds.   The contents are then allowed to separate into two distinct layers and the solid stopper is replaced by that carrying the syphon tube.   The solvent layer is syphoned over by applying gentle pressure to the open mouth - piece tube, and it is filtered through a small dry paper into a wide-mouthed squat flask of about 250 ml. capacity (CO_2 flask).   This extraction is repeated twice more.   A condenser is then fitted to the flask and the solvent is distilled off.   The fat remains behind in the flask, and after drying in a steam-oven for about 3 hours it is weighed.   It should be possible to dry to constant weight. It is officially recommended that when weighing flasks of this design, a similar flask should be used as a counterpoise.*

Fig. 5.—Extraction apparatus

The fat is next removed from the flask by dissolution in the solvent used for the extraction, the flask is again dried, cooled and weighed.   The loss in weight of the flask gives the weight of grease extracted.

   It is obvious that this method is applicable only to samples

* *Assoc. Official Agric. Chem., Standard Methods*, 4th Edn., 1936, p. 267.

—mostly trade wastes—which contain appreciable quantities of grease, i.e. of the order of 0·05–0·1 per cent. If the grease content is much less than this, as will normally be the case in ordinary sewages, a much larger portion of sample must be taken, and the determination may then be carried out most conveniently using an ordinary separating funnel of suitable size.

Combined Fat and Total Fat.

In addition to the last procedure, Wishart * described methods for the determination of combined and total fat in sewage. For the former, he acidifies the liquid remaining after the first extraction (he recommends ether as the solvent) with either hydrochloric or sulphuric acid and then repeats the extraction on this.

For total fat, the sample is acidified, stirred, and filtered, the fat being retained on the filter. The paper and fat are washed free from acid, dried at 100° C. and weighed. The fat is then extracted from this paper and residue in a Soxhlet apparatus. The paper and fat-free residue are again dried to constant weight, the difference between the first and final weighings being the weight of fat extracted from the sample. If desired, the solvent may be distilled off and the fat weighed directly as described above. It would appear that this is the better method.

Acidification with hydrochloric acid is to be preferred to acidification with sulphuric acid in the above methods.

It is essential to specify the solvent used when reporting the results.

* *J. Proc. Inst. Sewage Purif.*, 1935, **1**.

Boiler-Feed and Boiler-Waters

Many of the determinations already described are normally applied to the routine analysis of waters used in steam-raising plant, and the results obtained are often of special importance when regarded in the light of the conditions of operation. There are also several additional determinations which are of value for the examination of waters for this purpose, and these, together with a list of the other methods of particular interest, are included in this section. In spite of recent intensive research on boiler-feed water treatment and the maintenance of certain ratios of ions in the boiler water, the complexities of the mechanisms of scale formation and corrosion have still defied the efforts of the investigators to a large extent. It may be stated that the operation of every steam-raising plant is a minor—sometimes a major—research problem in itself, and optimum operating conditions can be determined only by careful, and regular, analysis of the feed, boiler-water, and condensate, coupled with a keen observation of the performance of the plant. The principles which are detailed in the following paragraphs are to be regarded as a guide only and not as inflexible rules. It will be observed that experts' opinions are not always in agreement.

Feed-water.

The mixture of feed-water and condensate supplied to a boiler should be completely free from bicarbonates. Kenyon * states that corrosion of steam and condensate lines is invariably due to free carbon dioxide, assisted by oxygen, and that this is derived from the bicarbonates present in the feed-

* *Food Manufacture*, 1941, **16**, 230.

water. Sodium bicarbonate has the same effect, so that natural
waters containing calcium and magnesium bicarbonates can-
not be treated satisfactorily by base-exchange softening alone.
It seems likely that the contention that corrosion under these
conditions is invariably due to carbon dioxide is rather an
over-statement.   Foaming, priming, or carry-over, which
results in an undesirable concentration of salts in the steam
and condensate, also causes corrosion, while ammonia in
steam attacks bronze valves and copper pipes.   Lancefield *
suggests the following limits:

Dissolved oxygen, 0·7 p.p.m. (0·5 ml. per litre).
Sodium chloride, 7·0 p.p.m. (0·5 grain per gallon).
Hardness, 28·0 p.p.m. (2 grains per gallon).
Caustic alkalinity, 7 to 10·5 p.p.m. (0·5 to 0·75 grain per
    gallon) expressed as $NaOH + Na_2CO_3$.

These limits may be relaxed somewhat for Lancashire boilers,
for which he suggests 35 p.p.m. (2·5 grains per gallon) total
hardness, and 49 to 56 p.p.m. (3·5 to 4 grains per gallon)
caustic alkalinity.   Turner † gives the following values for the
dissolved oxygen content of feed-waters used for locomotive
boilers:

Highest, 12·5 p.p.m. (7·9 ml. per litre).
Lowest, 7·3 p.p.m. (5·2 ml. per litre).
Average, 9·2 p.p.m. (6·6 ml. per litre).

These figures are averages over a long period; it is not sug-
gested that they are to be regarded as standards or permissible
limits.
    Concerning high-pressure boilers working at 600 lb. pres-
sure, Hewson ‡ gives limits of:

Dissolved oxygen, 0·01 ml. per litre (0·014 p.p.m.).
Electrical conductivity, not due to ammonia, 1 micromho per
    cm. cube at 20° C.
p_H, in the absence of ammonia, 7·3 to 7·5 at 20° C.

* *Food*, 1936, **5**, 389.
† " Corrosion of Boiler Tubes ", *Inst. Mech. Eng.*, London, 1942.
‡ *Chem. and Ind.*, 1941, **60**, 764.

Such boilers work on a closed-feed system. It is obvious that samples of this feed-water must be taken with the utmost care and that contact with air must be eliminated as far as possible. The p_H of such waters is determined by indicators; the p_H of the indicator solution should be adjusted so that it approximates to that of the water.

The p_H of boiler-feed water is often raised by the addition of caustic alkali. One object of this treatment is the suppression of corrosion. Hewson considers that a p_H of 9 is sufficiently high.

Corrosion is generally most severe in preheaters when the dissolved oxygen content of the feed-water is high and the p_H is low. Control of both p_H and of oxygen concentration may be effected by the addition of a mixture of soda ash and tannin. Sodium hexametaphosphate is very commonly added as an insurance against scale formation and corrosion, while starch is often preferred to tannin if oil is present in the water. Special methods for the determination of tannin and oil are described below.

Boiler-water.

The concentration of chlorides in a boiler-water is a valuable figure since the ratio

$$\frac{\text{Concentration of chloride in boiler-water}}{\text{Concentration of chloride in feed-water}}$$

gives a concentration index for the boiler-water. If the total solid concentration of the feed-water is known—as it should be—then the total solid content of the boiler-water is obtained from

$$\frac{(\text{Concentration of T.S. in feed}) \times (\text{Concentration Cl}' \text{ in boiler})}{(\text{Concentration Cl}' \text{ in feed})}.$$

The figure obtained is more or less approximate, according to the nature of the solids in the feed-water, but it is generally sufficiently accurate for the control of blow-down frequency.

A similar ratio giving information of a different character is

$$\frac{\text{Concentration of sulphate in boiler-water}}{\text{Concentration of sulphate in feed-water}}.$$

This ratio should be the same as the chloride ratio. If it is less, then sulphate must have been removed from solution, and the inference is that calcium sulphate scale is being deposited. On the other hand, if it is greater, the concentration of soluble sulphate in the boiler must have been increased by the dissolution of scale. Such an event often follows an improvement in feed-water treatment.

Of special interest and considerable controversy is the ratio of sulphate (as Na_2SO_4) to caustic alkalinity (as Na_2CO_3). Until fairly recently it was always held that a minimum value of 2 to 2·5 for this ratio was essential if the condition known as caustic embrittlement—inter-granular alkaline corrosion of the boiler steel—was to be prevented. It is more modern to attribute "caustic embrittlement" to inferior fabrication, but there is little doubt that the maintenance of the ratio has contributed towards longer boiler life in many cases of badly riveted or strained structures.

The permissible concentration of total solids in a boiler cannot be stated very definitely. The general rule appears to be that the higher the working pressure of the boiler, the lower should be the limit for total solids. Turner * gives 150–220 grains per gallon (2100–3080 p.p.m.) of dissolved salts as the limit for locomotive boilers, and Lancefield † suggests an upper limit of 500 grains per gallon (7000 p.p.m.) for stationary boilers with a relaxation to 840 grains per gallon (12,000 p. p. m. for Lancashire boilers (high-pressure boilers are not included in these suggestions). The caustic alkalinity, calculated as NaOH, should be about 10 per cent of the total dissolved solids.

The p_H of a boiler-water should be at least 10 if the calcium is to be efficiently precipitated as phosphate, but if it exceeds 11 carry-over is likely to be troublesome. There should always

be a reserve of soluble phosphate—if the feed-water is phosphate conditioned—in order to combine with any chance influx of soluble calcium salts.   Clark and Hunter * do not consider it practicable or safe to attempt to prevent scale-formation by maintaining a constant ratio of phosphate to sulphate in the boiler-water.

The role of silica in a boiler-water is somewhat obscure. If MgO and SiO_2 both exceed 5 p.p.m., a magnesium silicate scale is deposited, and this cannot be prevented by phosphate conditioning.   Silica is often found in deposits formed in turbines, and as it has not always been possible to ascribe this to carry-over, it has been suggested that silica is soluble in high-pressure steam.   The exact implication of this suggestion is not quite clear.

In waters which are not phosphate conditioned, calcium sulphate scale is avoided by maintaining a definite ratio of carbonate to sulphate in the boiler.   The value of the ratio depends on the operating pressure of the boiler; if the ratio CO_3''/SO_4'' is plotted on a graph against gauge pressure and the points $CO_3''/SO_4'' = 0.045$, pressure $= 100$ lb. per square inch, and $CO_3''/SO_4'' = 0.46$, pressure $= 400$ lb. per square inch, are joined by a straight line, the approximate optimum value of the ratio can be obtained for any intermediate pressure.   As normally determined, the concentration of the carbonate is obtained only by difference.   In the presence of organic matter and of other alkali salts such as phosphates and silicates, the figure for carbonate concentration may be considerably higher than the truth.   For this reason, greater reliance should be placed on the sulphate ratio mentioned above until the conditions under which

$$\frac{\text{Concn. Cl' in boiler}}{\text{Concn. Cl' in feed}} = \frac{\text{Concn. } SO_4'' \text{ in boiler}}{\text{Concn. } SO_4'' \text{ in feed}}$$

have been determined.   The corresponding value of CO_3''/SO_4'' may then be used for control purposes.   For further information the reader should refer to H. E. Jones's " Some Aspects of the Chemistry of Boiler-water ", *Fuel Economy Revue*, 1932.

Condensate.

Condensed steam should be pure water, but in practice it is not, owing to carry-over and corrosion. Probably the most informative figures are given by the electrical conductivity and the chloride determinations. The concentration of iron may sometimes give an indication of the corrosion which is taking place, but Haering * regards the chloride determination as the most useful.

Control Tests.

The following tests are suggested as the *minimum* requirements in connexion with steam-raising plant.

Daily determinations of:

(i) total alkalinity (cf. p. 12),
(ii) hardness (cf. p. 30),
(iii) magnesium hardness (cf. p. 32),
(iv) chloride (cf. p. 98 or preferably p. 99)

in the raw water. If this is softened, the softened water should be examined daily for

(i) total alkalinity,
(ii) hardness,
(iii) p_H (cf. p. 17),
(iv) caustic alkalinity (cf. p. 15),
(v) carbonate alkalinity (cf. p. 15).

The boiler-water should be examined daily for p_H, total, caustic, and carbonate alkalinity, and chloride.

Weekly determinations of sulphate should be made on both feed- and boiler-waters (cf. p. 100).

Sulphite in Boiler-feed Waters.

Sodium sulphite in some form is often added to boiler-feed waters to reduce their dissolved oxygen content. The following method may be used as a control test for this process.

Standard sodium thiosulphate, N/40 (cf. p. 43), is required

* *Ind. Eng. Chem.*, 1941, **33**, 1365.

and may be standardized against N/8 or N/80 potassium permanganate solution.   To a measured volume of the permanganate solution—50 ml. of the N/80 solution is convenient—add approximately 5 ml. of dilute sulphuric acid (25 per cent V/V) and an excess of potassium iodide. Titrate the iodine liberated with the sodium thiosulphate solution, using starch as indicator. An approximately N/40 solution of iodine is also required, 3·2 gm. per litre.

Pipette 10 ml. of the iodine solution into a conical flask of about 250 ml. capacity, and then add 5 ml. of glacial acetic acid. Measure 100 ml. of the sample in a pipette and run it slowly into the flask with the tip of the pipette held beneath the surface of the iodine, rotating the flask gently so as to mix the contents. Any sulphite present in the sample is oxidized by the iodine.   Then titrate the excess of iodine with the standard thiosulphate solution in the usual way.   Suppose this titration to require x ml. of the thiosulphate solution. Make a blank determination in which 100 ml. of distilled water, freshly boiled and cooled, are substituted for the sample. Then, if the blank determination requires v ml. of standard thiosulphate,

$$(v - x) \times 1\cdot58 = Na_2SO_3 \text{ parts per 100,000 in the sample.}$$

The sample for this determination should preferably be drawn specially for the purpose.   The bottle should be full and contact of the sample with air should be avoided as far as possible.   If the sample is hot when drawn, it should be cooled out of contact with air.   This is facilitated by filling a bottle with the sample previously cooled to about 60° C. and closing it with a rubber stopper through which passes a large S tube.

Electrical Conductivity.

It has become customary of recent years to measure the electrical conductivity of a water and to deduce therefrom the total concentration of dissolved solids.   The method can be made very accurate, and as it takes but a few minutes to complete a measurement it is very useful for the control of

boiler-water concentration. It may also be employed as a check on the mineral analysis of a water, when the total concentration of salts calculated from the electrical conductivity should agree with the value calculated from the concentrations of the various ions found by analysis within about 4 per cent. Further applications are to the routine examination of raw and treated waters, to the tracing of leaks in condensers, and in a different field, to the tracing of river pollution.

Practically any conductivity apparatus may be used, but a self-contained meter in a portable form—the Dionic Water Tester—is most convenient. A description of this apparatus is to be found in the catalogues of most laboratory furnishers.

Gustafson and Behrman * have investigated the relationship between electrical conductivity and the concentrations of the ions most commonly found in waters. They recommend the following procedure.

If necessary, dilute the sample with distilled water of conductivity not greater than $2 \cdot 5 \times 10^{-6}$ mhos so that the diluted sample contains 40–60 p.p.m. of dissolved solids (calculated as $CaCO_3$). Bubble air through the solution to remove any free carbon dioxide, and adjust the temperature to $25° \pm 3°$ C. Then determine the electrical conductivity of the solution and correct the result to $25°$ C. and multiply by the dilution factor. Gustafson and Behrman found that the conductivity could be calculated from the formula

$$E.C. = [HCO_3'] \times 0 \cdot 186 + [SO_4''] \times 0 \cdot 24 + [Cl']$$
$$\times 0 \cdot 249 + [NO_3'] \times 0 \cdot 241,$$

the concentrations of all the ions being calculated as equivalent $CaCO_3$ in p.p.m. A second useful formula given by these authors is

$$\frac{(\text{Conductivity} \times 10^5) - (\text{Alkalinity} \times 0 \cdot 186)}{0 \cdot 25}$$

$$= \text{non-carbonate solids (as } CaCO_3 \text{ in p.p.m.).}$$

* *Ind. Eng. Chem., Anal. Ed.,* 1939, **11**, 355.

In this formula the electrical conductivity is expressed in reciprocal ohms and the alkalinity in p.p.m. $CaCO_3$. To measure the conductivity for substitution in this formula, dilute the sample so that its conductivity lies between 9 and 13×10^{-5} mhos, adjust the reading to 25° C. and then correct for dilution.

The normal method of deduction of the total dissolved solids from the electrical conductivity is from a calibration curve on which the conductivity has been plotted against the total dissolved solids concentration as determined by accurate chemical analysis.

No doubt the use of recording instruments for the measurement of the electrical conductivity of boiler-feed waters will accompany the development of resin exchange-softeners.

Determination of Oil in Boiler- and Feed-waters.

The following method was described by Pringle.*

Fit a Winchester quart bottle with a cork and a siphon tube which reaches nearly to the bottom of the bottle. A well-fitting glass stopper is also required. Measure about 2·5 litres of the sample into the bottle and add 100 ml. of pure benzene (re-distilled A.R.) and 50 ml. of concentrated hydrochloric acid. Stopper the bottle and shake vigorously at intervals for 15 minutes. Introduce a hooked glass rod, on to which a 10-in. length of magnesium wire has been loosely wound, into the liquids and allow this to react with the acid solution for 15 minutes, moving the rod from time to time. The hydrogen thus evolved helps the separation of the benzene-water emulsion. Withdraw the rod and the wire and close the bottle with the cork carrying the siphon. Within a short time the liquids should separate into two layers, and after allowing sufficient time for them to clear of hydrogen, siphon over the bulk of the aqueous layer, leaving about equal volumes of benzene and water in the bottle. Transfer the rest of the liquids into a separating funnel, rinsing the bottle with 20 ml. of benzene and adding this to the bulk of the liquids in the funnel. Run to waste the rest of the aqueous layer and

wash the benzene with successive portions of distilled water until it is free from chloride. Transfer the benzene layer to a weighed flask and distil off the benzene. Dry the residue of oil in an oven at 100° C. until it is constant in weight. If possible, the flask should be counterpoised against a similar flask (cf. p. 114).

Determination of Tannins in Boiler- and Feed-waters.

Tannins are often added to boiler feed-waters with the object of reducing the concentration of dissolved oxygen, or to prevent the formation of hard scale, or to inhibit corrosion or caustic embrittlement. Until very recently, no altogether satisfactory method for the estimation of tannin in waters had been found. Some indication of the concentration is given by the " oxygen consumed test " (cf. p. 42), and also by the concentration of organic matter as derived from the volatile portion of the total solids. The limitations of such determinations are obvious. The method which follows was devised by Berk and Schroeder.[*] See also Rosenblatt and Pelnso.[†] It appears to be well adapted to routine control and should prove to be a valuable method.

Reagents required.

    (i) Tyrosine reagent. Dissolve 100 gm. of sodium tungstate, 20 gm. of phosphomolybdic acid, and 50 ml. of 85 per cent phosphoric acid in 750 ml. of water. Boil the mixture under reflux for 2 hours, cool, and make up to a litre.

    (ii) Saturated sodium carbonate. Dissolve 250 gm. of sodium carbonate in a litre of water, warming to effect solution, and allow the solution to stand at 20° C. Some crystals of the decahydrate should appear. Decant the clear supernatant solution and store in a bottle with a rubber stopper.

    (iii) Comparison solution. Weigh 5 gm. of the particular tannin extract in use and dissolve it in a litre of water.

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[*] *Ind. Eng. Chem., Anal. Edn.*, 1942, **14**, 456; cf. *Analyst*, 1942, **67**, 372.
[†] *J. Assoc. Off. Agric. Chem.*, 1941, **24**, 170.

Dilute 10 ml. of the solution to a litre. This solution then contains 50 p.p.m. of the extract. It is normally stable for about two months, but it will oxidize rapidly if it becomes contaminated with alkali.

(iv) Master standard solution. This is recommended as a check on the deterioration of the comparison solution (iii). Dissolve 1 gm. of pure tannic acid in a litre of water, and then dilute 25 ml. of the solution to 1 litre. The final solution thus contains 25 p.p.m. of pure tannic acid.

Procedure.

Measure a volume of the sample such as is estimated to contain about 0·15 mgm. of tannin or 1·0 mgm. of lignin, and run it into a Nessler glass. Turbid samples should be filtered. Add distilled water to make up to the 50-ml. mark. Prepare a number of standards from the comparison solution, 1 ml. of which, made up to 50 ml., gives a concentration of 1 p.p.m. Add 2 ml. of the tyrosine reagent to each tube and mix the contents. After 5 minutes add 10 ml. of saturated sodium carbonate solution, and after a further 10 minutes compare the blue colour of the unknown with the standards.

To check the comparison solution, simply treat this as the unknown and compare it with standards made up from the master standard solution of pure tannic acid.

Several precautions should be observed if the method is to be applied successfully. Owing to the rapid oxidation of tannins in alkaline solution the sample drawn for this analysis should be cooled, filtered as rapidly as possible, and then rendered neutral or slightly acid with hydrochloric acid. If this treatment results in the precipitation of some of the tannin, no harm will be done provided that the sample is shaken thoroughly before a portion is withdrawn for the determination. None of the inorganic substances normally present in boiler-water interferes with the determination, but the reaction is not specific for tannins, and phenols, if present, will interfere. In this event, a blank determination on the feed-water will enable a correction to be made.

CHAPTER XIV

The Expression of Results

It will be noticed—probably with a measure of annoyance —that no definite system of expressing results has been adopted in this book. Results appear almost indiscriminately in parts per million, parts per 100,000, and grains per gallon. The reason is that no universal system has yet been adopted, and no one can progress very far in water analysis without meeting results quoted in each of the above units and probably also in grains per U.S. gallon, English degrees of hardness (= ° Clark), and Continental degrees of hardness. Therefore, although the author's preference is for parts per million, it was thought necessary to point out the diverse systems in use.

Hypothetical Combinations.

The results of a mineral analysis of water are very often set out in terms of salts, e.g.:

Calcium carbonate ..	.. 14·0 grains per gallon.	
Calcium sulphate ..	.. 16·05	,, ,,
Magnesium sulphate	.. 10·54	,, ,,
Magnesium chloride	.. 1·85	,, ,,
Sodium chloride ..	.. 31·6	,, ,,
Iron oxide and alumina	.. 0·15	,, ,,
Silica	.. 0·49	,, ,,

These "hypothetical combinations" are arrived at quite simply by applying the following system. Iron and aluminium are calculated as Fe_2O_3 and Al_2O_3 and are reported as such. Silica is reported as SiO_2. The other metals are calculated as metals, and the non-metals are calculated as their most likely radicle or the corresponding acid. For example, the above

127

combinations were obtained from the following original analytical figures:

Calcium, 10·32   Magnesium, 2·60   Sodium, 12·80
Chlorine, 20·6   Sulphuric acid, 20·19   Silica, 0·49
Iron oxide and alumina, 0·15   Carbonic acid, 8·65
(All results in grains per gallon.)

The metals were then "combined" with the negative radicles in the following order:

Metal	Negative radicle
Calcium	Carbonate
Magnesium	Hydroxide
Sodium	Sulphate
Potassium	Nitrate
	Chloride

Dividing each metal and each radicle, or acid, by its equivalent weight we obtain:

Metal	Acid or radicle
Calcium, 0·515	Carbonic, 0·279
Magnesium, 0·214	Hydroxide, nil
Sodium, 0·557	Sulphuric, 0·411
Potassium, nil	Nitric, nil
	Chloride, 0·580

(These values are now *grain*-equivalents per gallon.)

The calcium is more than sufficient to combine with all the carbonic acid, hence the concentration of calcium carbonate is 0·279 grain-equivalents per gallon, or 14·0 grains per gallon.   This leaves 0·515 — 0·279 grain-equivalents of calcium = 0·236.   As there is no hydroxyl, this must be calcium sulphate. There is more sulphuric acid than is necessary to combine with the whole of this calcium, so the concentration of calcium sulphate is 0·236 × the equivalent weight of calcium sulphate = 16·05 grains per gallon.   The residual sulphuric acid is 0·411 — 0·236 grain-equivalents per gallon = 0·175.   As all the calcium has been accounted for, this sulphuric acid is combined with the magnesium. Hence the concentration of magnesium sulphate is 10·54 grains per

gallon and $0.214 - 0.175 = 0.039$ grain-equivalents of magnesium are left to be combined in their turn with the chloride, i.e. the concentration of magnesium chloride is 1.85 grains per gallon. The residual equivalents of chloride $= 0.541$, which is a little less than is required to combine with the whole of the sodium, from which the concentration of sodium chloride is calculated as 31.6 grains per gallon. This leaves a small residue of sodium, which would be expected in view of the concentration of silica in the water.

This method of reporting results is of value as a check on the analysis, as serious discrepancies are revealed which might easily pass unnoticed in a simple list of concentrations of elements and radicles. It gives, too, a superior picture of the composition of the water. The various salts are classifiable into incrustants—scale-forming materials—and non-incrustants. The calcium and magnesium salts are incrustants; so also are silica and iron and aluminium oxides. Salts of the alkali metals are non-incrustants.

For boiler-feed waters, a valuable figure to report is the total of scale- and sludge-forming materials. This is the sum of the calcium carbonate, calcium hydroxide, calcium sulphate, iron and aluminium oxides, silica, and magnesium hydroxide. For this purpose, magnesium salts are calculated to the equivalent weight of hydroxide, as the p_H of the water in the boiler should be high enough to precipitate magnesium in this form. In the example quoted, the sum of the scale- and sludge-forming materials is $14.0 + 16.05 + 6.25 + 0.49 + 0.15 = 36.94$ grains per gallon.

APPENDIX

TABLE 8

DRINKING-WATER ANALYSIS

Appearance: Clear and colourless with few small particles suspended.

Free and saline ammonia (as nitrogen) ..	0·001	part/100,000
Albuminoid ammonia (as nitrogen) ..	0·003	,,
Chlorides (as chlorine)	1·50	,,
Nitric nitrogen	0·100	,,
Total solids (including suspended solids)	9·40	,,
Suspended solids	Trace	
Oxygen absorbed from N/80 KMnO$_4$ in 4 hours	0·05	,,
Temporary hardness	0·50	
Permanent hardness	4·00	
Total hardness	4·5	
Sulphates (as SO$_3$)	0·70	,,
Calcium (as CaO)	2·30	,,
Magnesium (as MgO)	0·58	,,
Iron (as Fe$_2$O$_3$)	0·05	,,

Hardness expressed as degrees Clark, i.e. as CaCO$_3$ per 70,000.

TABLE 9

ANALYSES OF EFFLUENTS FROM PERCOLATING FILTERS
AFTER REMOVAL OF HUMUS

	A	B	C	D
Oxygen absorbed in 3 min. ..	1·53	1·40	—	0·62
Oxygen absorbed in 4 hr. ..	4·04	3·73	1·02	1·45
Chlorides	18·4	17·5	—	12·7
Ammonia nitrogen (free and saline)	2·70	3·80	—	0·73
Albuminoid nitrogen	0·13	0·34	—	0·12
Nitrous nitrogen	0·43	0·16	—	—

		A	*B*	*C*	*D*
Nitric nitrogen	.. ..	3·10	3·60	0·90	4·20
Biochemical oxygen demand, 5 days	.. ..	1·49	2·23	0·83	—
Suspended solids	.. ..	—	—	—	5·4

Results returned as parts per 100,000.
Oxygen-absorbed tests carried out with N/80 KMnO$_4$.
In spite of their high oxygen-absorbed values, samples
   A and B were stable; this would be the result of their
   high nitrate content.

TABLE 10

ANALYSES OF EFFLUENTS FROM PERCOLATING FILTERS

Ammonia N	.. ..	0·08	0·40	1·83	1·32	1·23
Albuminoid N	.. ..	0·08	0·14	0·20	0·25	0·18
Nitric N ..	.. ..	5·8	5·3	—	2·7	3·5
Oxygen absorbed in 4 hr.	..	0·83	1·33	2·31	2·64	1·64
Chlorides ..	.. ..	15·0	13·5	12·6	14·2	11·9
p_H	.. ..	6·7	7·0	6·9	7·8	7·2
Alkalinity ..	.. ..	—	13·1	—	20·1	20·2
Suspended solids ..	.. ..	2·7	2·6	2·8	2·1	4·1
B.O.D., 5 days ..	.. ..	0·52	1·38	5·2	4·3	2·0

Results in parts per 100,000.
Alkalinity (as CaCO$_3$), to methyl-orange.

TABLE 11

ANALYSES OF SETTLED DOMESTIC SEWAGE AND THE
EFFLUENT FROM AN ACTIVATED SLUDGE PLANT

	Settled Sewage	Effluent
Oxygen consumed in 4 hr.	3·90	1·07
Oxygen consumed in 3 min.	1·43	0·25
Oxygen consumed after incubation ..	—	0·23
Free and saline ammonia (as N) ..	1·89	1·83
Albuminoid nitrogen	0·49	0·15
Nitrous nitrogen	—	trace
Nitric nitrogen	—	0·06
Biochemical oxygen demand	12·68	1·15
Suspended solids	16·1	1·53

(From the *Annual Report, City of Manchester Rivers
Department*, 1932.)
Results in parts per 100,000.

SOME MISCELLANEOUS TRADE EFFLUENTS

Spent dye from felt hat manufacture.

        Appearance: Clear, deep blue.
        Sediment: Nil.
        Odour: Nil.
        Reaction: Acid to litmus.
        Suspended solids: Nil.
        Oxygen consumed in 4 hr., $N/80$ $KMnO_4$ test: 17·0 parts
            per 100,000.
        Acidity, calculated as H_2SO_4: 80·0 parts per 100,000.

Hat manufacture, collected effluent (*settled and screened*).

        Appearance: Turbid, dirty grey.
        Sediment: Fine black.
        Odour: Oily.
        Reaction: Acid to litmus.
        Suspended solids: 49·4 parts per 100,000.
        Oxygen consumed in 4 hr., $N/80$ $KMnO_4$ test: 5·5 parts
            per 100,000.
        Acidity, calculated as H_2SO_4: 71·3 parts per 100,000.

Sulphur dye waste, wash water.

        Appearance: Opaque, deep green.
        Odour: Hydrogen sulphide.
        Reaction: ·Alkaline to litmus.
        Suspended solids: Nil.
        Oxygen consumed in 4 hr., $N/80$ $KMnO_4$ test: 208 parts
            per 100,000.
        Alkalinity, calculated as equivalent H_2SO_4: 51·7 parts
            per 100,000.

Tannery waste, after settlement in continuous flow tank.

        Appearance: Turbid, deep brown.
        Sediment: Black.
        Odour: Faint.
        Reaction: Acid to litmus.
        Suspended solids: 38·4 parts per 100,000.
        Oxygen consumed in 4 hr., $N/80$ $KMnO_4$ test: 155·5
            parts per 100,000.
        Acidity, calculated as H_2SO_4: 85·2 parts per 100,000.

Laundry waste.

> Appearance: Opalescent.
> Sediment: White.
> Odour: Soap.
> Reaction: Alkaline to litmus.
> Suspended solids: 28·2 parts per 100,000.
> Oxygen consumed in 4 hr., $N/80$ $KMnO_4$ test: 14·9 parts per 100,000.
> Alkalinity: Trace.

Chemical waste from pigments manufacture.

> Appearance: Opaque, turbid, crimson.
> Sediment: Light, crimson.
> Liquid: Clear, faintly yellow.
> Odour: Faint aromatic.
> Reaction: Alkaline to litmus.
> Suspended solids: 80·0 parts per 100,000.
> Oxygen absorbed in 4 hr., $N/80$ $KMnO_4$ test: 27·5 parts per 100,000.
> Alkalinity, calculated as equivalent H_2SO_4, 25·9 parts per 100,000.

Food Processing wastes:

(a) Potato washing, sampled after settlement in a series of baffled, continuous-flow tanks.

> Appearance: Cloudy brown.
> Sediment: Brown; much colloidal matter.
> Odour: Sour.
> Reaction: Neutral to litmus.
> Suspended solids: 93·3 parts per 100,000.
> Oxygen consumed in 4 hr., $N/80$ $KMnO_4$ test: 9·0 parts per 100,000.

(b) Cannery waste (processed peas).

> Appearance: Slightly cloudy, pale green.
> Sediment: Few coarse solids; some colloidal matter.
> Odour: Strong; decayed vegetation.
> Reaction: Acid to litmus.
> Suspended solids: 35·0 parts per 100,000.
> Oxygen consumed in 4 hr., $N/80$ $KMnO_4$ test: 240·0 parts per 100,000.
> Acidity, calculated as H_2SO_4: 21·5 parts per 100,000.

> *Note.*—The sample deteriorated (by fermentation) very rapidly. The above results were obtained within 24 hr. of the sample being taken.

TABLE 12

ANALYSIS OF AN INDUSTRIAL SEWAGE

Oxygen absorbed in 4 hr. at 80° F. (acid N/80 KMnO$_4$ test)	127·0 p.p.m.
Oxygen absorbed in 3 min. at 80° F. (acid N/80 KMnO$_4$ test)	48·5 p.p.m.
Chloride	142·0 p.p.m.
Alkalinity (calculated to equivalent H$_2$SO$_4$)	211·0 p.p.m.
Suspended solids	354·0 p.p.m.
Free and saline ammonia (as N)	29·4 p.p.m.
Albuminoid nitrogen	12·3 p.p.m.
Biochemical oxygen demand (5 days at 65° F.)	465·0 p.p.m.
p_H	8·2

TABLE 13.—TYPICAL ANALYSES OF WATERS USED FOR LOCOMOTIVE BOILER-FEED IN RECENT YEARS. Expressed as grains per Imperial gallon, i.e. parts per 70,000

	1 Eastern Counties	2 North Midlands		3 London		4 South-east Midlands		5 Leeds	6 Scotland	7
	Raw	Raw	Soft	Raw	Soft	Raw	Soft	Raw	Raw	Raw
Total dissolved solids	79·6	66·00	54·07	26·4	12·0	35·10	21·69	7·45	12·1	1·55
Calcium	10·32	6·46	0·60	6·83	0·80	5·82	0·50	0·93	1·09	0·10
Magnesium	2·60	3·86	0·16	0·37	0·16	0·62	0·38	0·17	0·33	0·07
Sodium	12·80	10·71	18·83	1·46	2·76	6·55	6·91	0·85	2·07	0·25
Iron oxide and alumina	0·15	0·06	0·04	Trace	Trace	0·03	0·11	0·25	—	0·03
Silica	0·49	1·40	0·46	0·76	0·27	0·31	0·40	1·27	0·84	0·04
Chlorine	20·6	11·20	11·60	1·9	1·65	5·40	5·20	1·05	3·00	0·50
Sulphuric acid	20·19	21·38	19·71	3·69	2·62	5·02	5·75	2·17	1·97	0·22
Nitric acid	—	Trace	Nil	1·58	0·83	Nil	Nil	0·16	1·12	Trace
Carbonic acid	8·65	10·43	1·35	8·40	1·76	11·10	2·10	0·60	0·84	0·08
Hydroxyl	—	—	1·32	—	—	—	0·34	—	—	—
pH value	7·6	7·1	11·0	7·5	9·5	7·6	11·0	6·8	6·5	6·7
Alkalinity (as calcium carbonate)	14·42	17·38	6·13	14·00	2·94	18·50	4·50	1·00	1·4	0·14
Temporary hardness (calculated)	14·5	17·38	—	14·0	2·6	17·13	2·83	1·00	1·4	0·14
Permanent hardness (calculated)	22·0	14·85	2·17	4·6	0·1	—	—	2·04	2·7	0·40
Total hardness (calculated)	36·5	32·23	2·17	18·6	2·7	17·13	2·83	3·04	4·1	0·54
Calcium hydroxide	—	—	1·11	—	—	—	0·74	—	—	—
Calcium carbonate	14·42	16·15	—	14·00	2·00	14·55	0·25	1·00	1·40	0·14
Magnesium carbonate	—	1·04	—	—	0·56	2·17	1·33	—	—	—
Calcium sulphate	15·47	—	—	4·18	—	—	—	1·80	1·80	0·14
Calcium chloride	—	17·80	—	—	—	—	—	—	—	—
Magnesium sulphate	1·59	—	—	0·93	—	—	—	0·85	0·88	0·15
Magnesium chloride	1·11	—	—	0·71	—	—	—	—	0·59	0·16
Magnesium hydroxide	—	—	0·39	—	—	—	—	—	—	—
Sodium carbonate	—	—	1·37	—	0·28	1·45	1·77	—	—	—
Sodium sulphate	—	10·57	2·39	—	3·88	7·43	8·51	0·33	—	—
Sodium chloride	32·74	18·48	29·17	2·26	2·72	8·91	8·58	1·73	4·22	0·63
Sodium nitrate	—	—	19·14	2·17	1·14	Nil	Nil	0·22	1·53	Trace
Iron oxide and alumina	—	Trace	Nil	—	—	0·03	0·11	0·25	—	0·03
Silica	—	1·40	0·46	—	—	0·31	0·40	1·27	0·84	0·04
Scale and sludge-forming matter:—										
Grains per gal.	36·81	26·91	2·00	19·83	2·66	16·38	2·42	4·73	4·83	0·52
Lb. per 1000 gal.	5·26	3·84	0·29	2·83	0·38	2·34	0·35	0·68	0·69	0·07

CONVERSION FACTORS

	Grains per gal.	Parts per 100,000	P.p.m.	°Clark	Grains per U.S. gal.	French° hardness.	German° hardness.
Grains per gal. ..	1	1·43	14·3	1	0·829	1·43	0·8
Parts per 100,000	0·7	1	10	0·7	0·583	1	0·56
P.p.m.	0·07	0·1	1	0·07	0·058	0·1	0·056
°Clark	1	1·43	14·3	1	0·829	1·43	0·8
Grains per U.S. gal. ..	1·2	1·71	17·1	1·2	1	1·71	0·96
French° hardness ..	0·7	1	10	0·7	0·583	1	0·56
German° hardness ..	1·25	1·78	17·8	1·25	1·04	1·78	1

All degrees of hardness (except German degrees) expressed in terms of $CaCO_3$.

To convert a result expressed in one unit into another, find the existing unit in the left-hand column and multiply by the factor given under the appropriate column head; e.g. to convert "French degrees of hardness" into "grains per U.S. gallon", multiply by 0·583.